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RAY T. BAYLESS, *Editor*

Vol. XXII August, 1934 No. 8

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HEAT TRANSFER RATES IN FUEL-FIRED FURNACES

By M. H. Mawhinney

Abstract

A great deal has been written in recent years on the subject of theoretical heat transmission and the development of mathematical formulas for calculating the overall transmission of heat, particularly in boiler and still furnaces. These formulas become so involved and require such a large number of assumptions that their application to metallurgical furnaces seems hopeless.

In boiler and still furnaces the heat receiving surface is a fixed quantity, and certain assumptions can be made within the necessary limits of accuracy. In metallurgical furnaces, however, the material to be heated varies widely in form and size and is handled in a variety of ways through the furnaces of all sizes and shapes, which makes the application of mathematical formulas practically impossible.

This paper attacks this problem in a quite different manner, and commences by summarizing experimental data which has been collected from a number of actual furnace installations of various kinds, where facilities were available for the determination of temperatures and other measurements.

From this collection of data the overall heat transmission coefficients are calculated and a proposed method is advanced for the rating of metallurgical furnaces in place of the commonly used method of rating expressed in pounds of material heated per square foot of hearth per hour. The proposed method takes into account the relationship between weight of steel heated and area of receiving surface, which in many cases must be considered if a furnace of the correct size is to be selected.

The application of this data in the prediction of heating cycles in furnaces is also described, which is becoming of increasing importance with the growth of involved metallurgical processes requiring accurate heating curves of varying shapes.

This paper was presented by M. H. Mawhinney, fuel engineer, The Electric Furnace Company, Salem, Ohio. It formed a part of the Heat Transfer Symposium, sponsored by the American Society of Mechanical Engineers in cooperation with the American Society for Metals, at their New York meeting on December 5, 1933. Manuscript received November 23, 1933.

THE purpose of this paper is to study the rate of heat transfer in fuel-fired furnaces and to propose a method of determining the furnace size necessary to heat a given quantity of steel pieces of known size and shape by the application of experimental data included in the paper. Much has been written on the subject of theoretical heat transfer, and progress has been made toward the solution of some problems, such as the transfer of heat in boiler and still furnaces, where the receiving surface is a constant and known quantity. However, in the case of metallurgical furnaces, where the size and shape of heated pieces, temperatures, radiating areas and method of firing all vary widely, the theoretical method becomes so complicated and requires so many assumptions that the practical application is yet of little value.

In the practice of metallurgical furnace design the generally accepted method of determining furnace size is to use some empirical rule limiting the number of pounds of steel which may be heated per square foot of furnace hearth per hour. One such rule is that 30 pounds of steel may be heated per square foot of hearth per hour for heat treating, 60 pounds for rough annealing, 80 pounds for forging and rolling, etc. Such a device recognizes to some extent the effect of temperature uniformity required in the product, allowable temperature head and furnace temperature, but takes no account whatever of the relative area exposed to the heat in stock of different sizes and shapes.

In an effort to work out a practical method to include the relation between the stock dimensions and the rate at which it can be heated, the author has made tests on a number of actual furnace installations of different kinds, the results of which are summarized in Table I. All tests were made with the furnace in steady production, and in each case the rate of heating was determined by dividing the pounds of steel heated per hour by the hearth area in square feet. The rate of heat absorption by the steel was found by dividing the heat content of the steel heated per hour to known temperature by the constant effective heat receiving area of steel in the furnace. This area is that of the steel in the furnace which is so located as to be able to receive heat by radiation or convection. For example, in a furnace in which 4½-inch square billets are pushed in grooves, it was estimated that three of the four sides of the billets were effective. Similarly, where sheets are supported on piers or chains just above the furnace hearth, only one half of the

Table I
Relationship Between Stock Dimensions and the Rate of Heating

Table I

Relationship Between Stock Dimensions and the Rate of Heating

Furnace Number	Fuel	Purpose of Furnace	Product Heated	Type of Furnace	Preheat, Degrees Cold Stock	B.t.u. Per Lb.	Final Control Temp.	Final Temp. Product	Hearth Area Ft.²	Effect. Area Product in Fce.	$K = AH_1/AR$	Pounds Per Hr. Total	Mean Furnace Temp.	Mean Temp. of Product	Diff. in Mean Temp.	Heating Rate Lbs./Ft.² Per Hr.	Coeff. B.t.u./Ft.² Per Hr. Per Deg.
1	Oil	Forging	2½"x2½" Billets	Pusher	....	380	2400	2300	108	175	.62	4500	2280	1560	720	41.6	13.6
2	Oil	Forging	2½"x2½" Billets	Pusher	....	345	2500	2300	108	175	.62	8960	2329	1476	853	83.0	20.7
3	Nat. Gas	Forging	4¼"x4¼" Billets	Pusher	....	350	2300	2200	90	127	.71	3420	2200	1440	760	38.0	12.4
4	C.O. Gas	Forging	2" Dia. Bars	Batch	....	350	2300	2200	22.5	29.5	.76	1800	2250	1420	830	80.0	25.8
5	Oil	Rolling	4"x4" Billets	Batch	....	330	2200	2150	94	197	.48	3160	1840	1310	530	33.7	10.0
6	Nat. Gas	Annealing	20" Dia. Rolls	Car	....	270	1750	1700	440	572	.77	3040	1120	970	150	6.9	9.6
8	Oil	Forging	10"x4½"x2½" Bars	Rotary	....	360	2400	2300	50	40.2	1.24	2200	2400	1500	900	44.0	18.9
9	Nat. Gas	Normalizing	Stainless Sheets	Rotary	....	300	2040	1900	555	512	1.08	3220	2030	1250	780	5.8	2.4
10	Electric	Hardening	Rollers in Pans	Pusher	....	240	1550	1500	26	51.5	.50	850	1330	1010	320	32.7	12.4
11	Oil	Hardening	Axles	Pusher	....	210	1400	1380	156	459	.34	3770	1350	1160	190	24.2	8.7
12	Nat. Gas	Normalizing	Axles	Walking Beam	....	260	1650	1600	69.5	114	.61	2040	1556	1436	450	29.3	10.3
13	Oil	Drawing	Axles	Pusher	....	130	1060	1020	150	470	.32	4020	994	850	144	27.0	7.7
14	Nat. Gas	Drawing	Axles	Walking Beam	....	93	825	800	86.6	140	.62	2040	750	560	190	23.5	7.1
15	Nat. Gas	Annealing	20" Dia. Retorts	Car	....	220	1380	1350	329	708	.47	1925	1291	1134	157	5.9	3.8
16	Nat. Gas	Normalizing	Strip Steel	Chain	....	270	2000	1700	75	81	.93	4000	1800	1120	680	53.3	19.5
17	Electric	Normalizing	Strip Steel	Roller Hearth	....	270	2100	1700	24	36	.67	2000	2000	1120	880	83.3	15.0
18	Nat. Gas	Normalizing	9⅝" Pipes	Sloping Hearth	....	270	1750	1700	1480	2880	.51	22500	1400	1110	290	15.2	7.3
19	Prod. Gas	Rolling	12"x12" Blooms	Pusher	....	340	2200	2100	855	1210	.71	50000	1900	1250	650	58.0	21.5
20	Nat. Gas	Annealing	3"x22'x4" Boxes	Pusher	....	270	1600	1550	138	276	.50	3036	1550	1083	470	22.0	6.6
21	Nat. Gas	Hardening	¾"x25' Rods	Chain	....	240	1600	1550	320	295	1.08	2930	1287	925	362	9.2	6.6
22	Nat. Gas	Drawing	¾"x25' Rods	Chain	....	130	1060	1020	320	295	1.08	1220	857	636	221	3.8	2.4
24	Nat. Gas	Forging	¼"x2¼" Slugs	Batch	....	300	1985	1950	10	23.6	.42	253	1950	1662	288	25.3	11.2
25	Nat. Gas	Patenting	⅝" Dia. Wire	Strands	....	270	1850	1600	360	79	4.6	3870	1750	835	915	10.8	14.5
26	Nat. Gas	Rolling	9"x9"x18' Blooms	Pusher	....	340	2200	2100	1380	2340	.59	100000	1850	1250	600	73.0	24.2
					Preheated Stock												
P1	Oil	Forging	44" Dia. Ingots	Batch	800	260	2350	2200	56.7	130	.44	1480	2100	1934	166	26.0	18.0
P2	Oil	Annealing	20" Dia. x 18' Pipes	Chain	1000	150	1750	1720	745	754	.99	50000	1660	1360	300	67.2	33.3
P3	Nat. Gas	Hardening	Axles	Walking Beam	1000	110	1580	1550	53.2	76	.70	2040	1550	1420	130	38.2	22.7
P4	Electric	Annealing	Steel Discs	Roller Hearth	1000	110	1550	1525	62.5	88	.71	2460	1500	1350	150	39.2	20.5
P5	Oil	Normalizing	Cranks	Pusher	1200	70	1650	1600	97	165	.59	5510	1603	1518	85	57.0	27.4
P6	Electric	Reheating	Forgings	Batch	1750	130	2450	2300	10	14.6	.69	818	2450	2280	170	81.8	42.8

bottom can be considered as effective. In continuous billet furnaces of the split flame type, just the top and bottom of the billets are effective. In many cases, however, the entire area of the stock is effective.

The mean temperature head in the furnace is the average temperature of the surface of the steel for the time it is in the furnace,

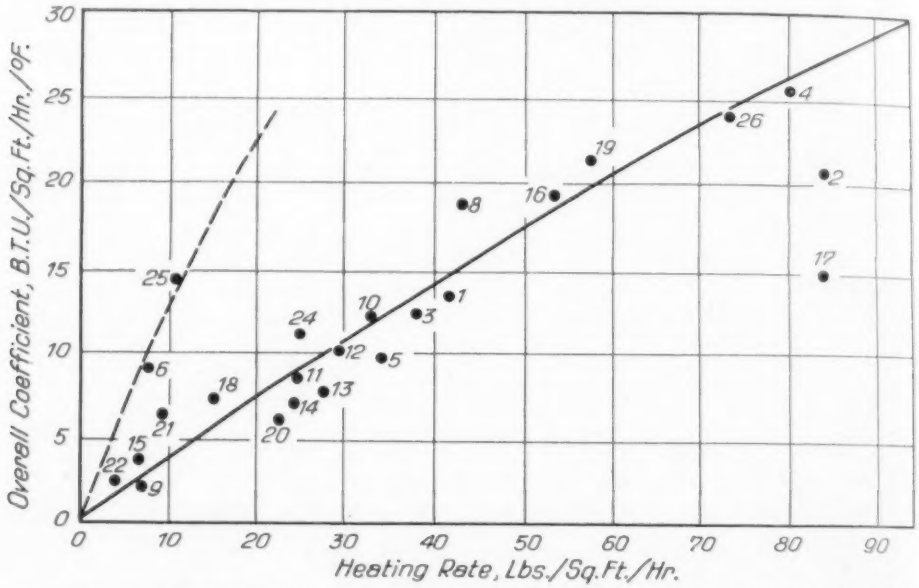


Fig. 1—Curves Showing the Values of Overall Coefficients of Heat Transfer Plotted Against the Rate of Heating. See Table I.

found in most cases by thermocouples, subtracted from the average furnace temperature. The overall coefficient of heat transfer, in B.t.u. per square foot of effective steel area in the furnace per hour per degree mean temperature head is found by dividing the above rate of heat absorption by the mean temperature head. In Table I those furnaces in which the steel enters the furnace with some preheat were separated from those heating cold stock, and will be discussed separately in the paper.

Relation Between Heating of Cold Stock and the Overall Coefficient

When the values of the overall coefficient from Table I are plotted against the rate of heating, they show an apparently consistent relation, as illustrated by Fig. 1. Those few points which depart widely from the curve are found upon examination to be unusual cases of heating practice. For example, point 6 is for a batch furnace in

which very large pieces are heated for a long time, so that the surface of the steel is at temperature for a long time, with consequent low mean temperature head and high values for the coefficient. The dotted curve indicates the possible relation for this unusual class of heating. Point 25 is for a wire patenting furnace, where the

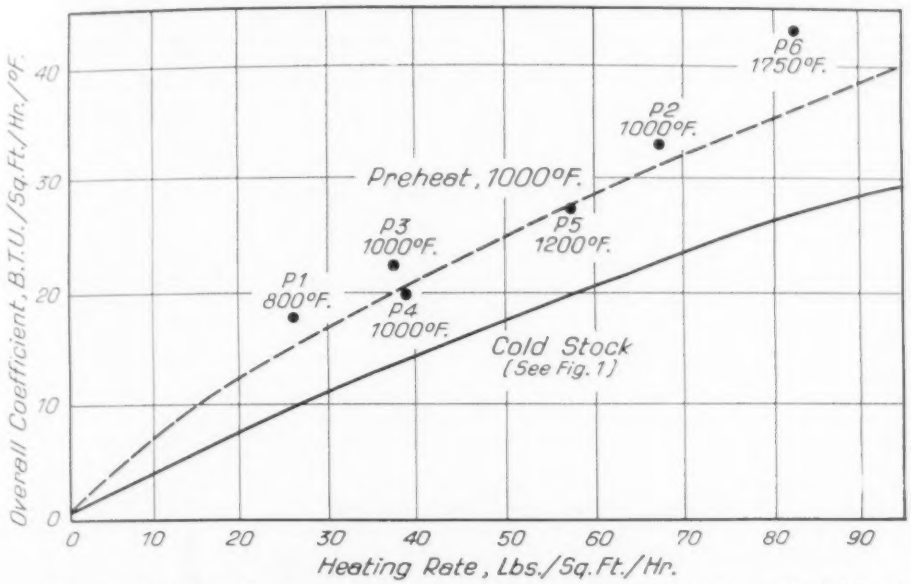


Fig. 2—Relation Between Overall Coefficients of Heat Transfer and Rate of Heating. See Table I.

ratio between hearth area and the heat receiving surface (K in this paper) is unusually large.

The accumulation of further data will be necessary to establish the exact position of the curve of Fig. 1, but the data available, covering a considerable variety of furnace designs, shows a very definite and consistent relation to exist.

The Effect of Preheated Stock

Heating steel which is already partially heated is a requirement of many furnace installations and is a condition under which it is particularly difficult to determine the possible heating rates. The number of cases of this type available for study was too small to supply sufficient data for any definite conclusions, but those available have been listed in Table I. The method of calculation of heating rate, heat absorption and overall coefficient was the same as for cold stock except that the net heat content obtained in the furnace is the difference between the heat content at the final steel temperature

and the heat content when the steel enters the furnace. Also the mean temperature of the steel is higher with preheated stock.

The relation between overall coefficient and rate of heating is shown in Fig. 2, on which the curve for cold stock is repeated from Fig. 1. The overall coefficients are clearly higher with preheated stock, and the probable curve for a preheat of 1000 degrees Fahr. is shown by the dotted line. The effect of preheating on the mean temperature

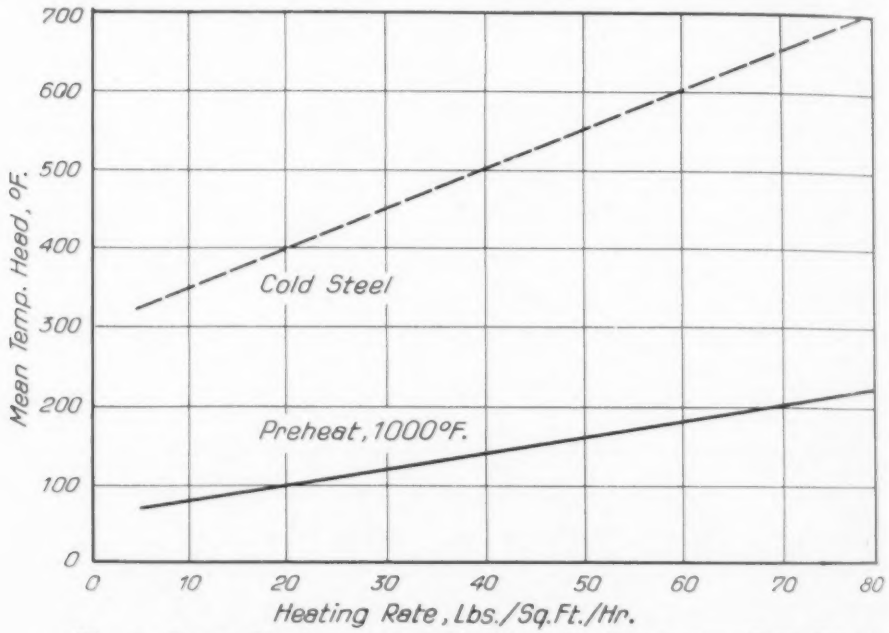


Fig. 3—Curves Showing the Probable Lines for Temperature Head Plotted Against Rate of Heating.

head in a furnace can be clearly illustrated by the examples of 12 and P3 in Table I, which were identical furnaces heating an identical product. In the case of furnace 12, the stock entered the furnace cold, and the heating rate was 29.3 pounds per square foot per hour, while in furnace P3, the stock entered at 1000 degrees Fahr. preheat and was heated at the rate of 38.2 pounds per square foot per hour. Fig. 3 shows the probable lines for temperature head plotted against rate of heating in the two cases and illustrates the difference in temperature head requirements caused by the preheating of the steel.

Determination of Furnace Size

Although the values of overall coefficient given above are of possible value in the development of the theoretical study of heat transfer, they are of practical use only to indicate whether a furnace

already designed will operate with excessive temperature head. With the coefficient from Fig. 1 for a known rate of heating and with known total heat per hour and steel area in the furnace, the temperature head is:

$$\text{Mean temperature Head} = \frac{\text{B.t.u. per hour}}{\text{exposed steel area} \times \text{coefficient}}$$

As an example, suppose that a furnace 4 feet wide and 20 feet long has been designed to fine heat treat pressed steel bowls at 1600

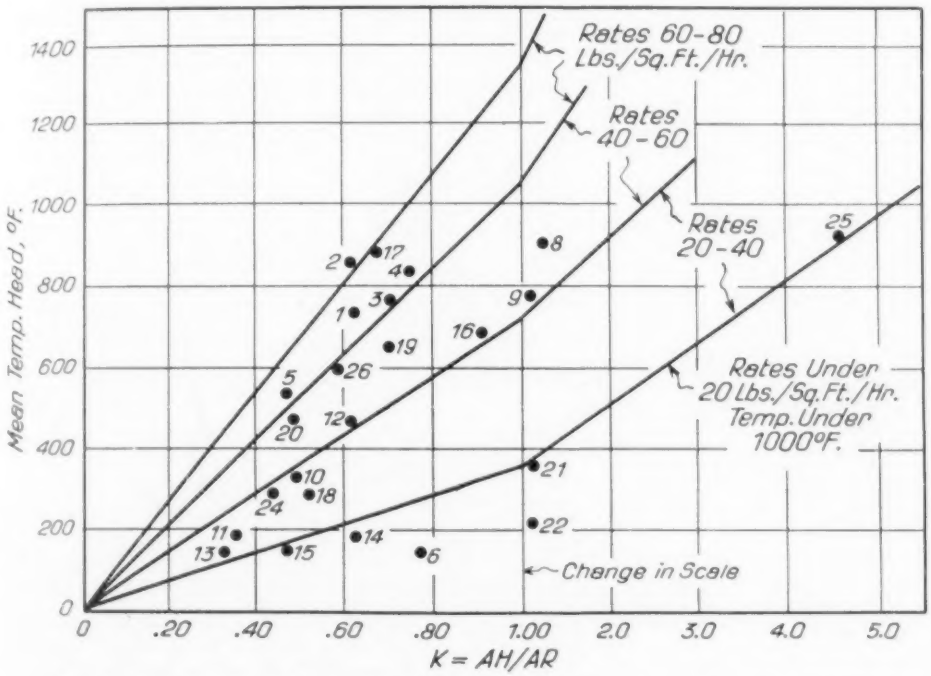


Fig. 4—Curves for Cold Stock Showing the Relationship Between Temperature, Rate of Heating and K. See Table I.

degrees Fahr. at the usual rate of 30 pounds per square foot of hearth per hour. The production is 2400 pounds per hour, and the furnace will hold 20 pieces, each with an exposed area of 13.8 square feet inside and out, or a total steel area in the furnace of 276 square feet. The total heat absorbed is 2400 pounds per hour $\times$ 240 B.t.u. per pound, or 576,000 B.t.u. per hour. From Fig. 1, the coefficient at the rate of heating of 30 pounds per square foot per hour is 11.0 B.t.u. per square foot per hour per degree Fahr. Then:

$$\text{Mean temperature Head} = \frac{576{,}000}{276 \times 11.0} = 189 \text{ degrees Fahr.}$$

Table II

Operation	Maximum Temperature Head, Degrees Fahr.
Annealing very large pieces	150
Forging large pieces, like rolls	180
Low temperature tempering	200
Fine heat treating	300
Fine heat treating where hearth is not well covered, like rods on wide centers	400
Rough heat treating, or high temperature, like stainless	500
High temperature forging or rolling, medium rates of heating	650
Forging or rolling, high rates of heating	850
Continuous normalizing sheets and strip, flash heating	800
Wire patenting, continuous	900
Preheated Stock	
Fine heat treating, preheated to about 1000 degrees Fahr.	150
Rough heat treating	300

This value is well below the permissible temperature head for this class of heating, as explained below, and it is indicated that such product may be heated at a higher rate, as might be suspected where the area is relatively large for the weight of the piece.

Where the area of furnace is to be found, other methods must be employed. For this purpose, the information in Table I has been combined in Fig. 4 for cold stock to show the relation between temperature head, rate of heating and

$$K = \frac{\text{hearth area}}{\text{effective steel area in the furnace}}.$$

The lines in this illustration divide the points into groups with respect to rate of heating, which groups are found to be quite consistent for the data available.

The value of K can be determined from the known area of the pieces to be heated and the number of pieces which may be loaded per square foot of hearth in the furnace. It is known that for various kinds of heating the mean temperature head should not exceed a maximum figure, which, from the author's experience, are given in Table II.

By the use of Table II and the values of Fig. 4, it is proposed to find the hearth area required in any case, as illustrated by the following examples:

Example 1

Suppose that in the case of the pressed steel bowls already discussed it is desired to find the actual area of hearth required to

properly heat treat 2400 pounds of this product per hour. Then since we have already stated that the furnace 4 feet × 20 feet will hold 20 pieces of 13.8 square feet exposed area each,

$$K = \frac{4 \times 20}{20 \times 13.8} = 0.29$$

Allowable temperature head for fine heat treating is 300 degrees Fahr. from Table II. Then, from Fig. 4, the allowable rate of heating in this case is at least 40 pounds per square foot per hour. The maximum hearth area required is then

$$\frac{2400}{40} = 60 \text{ square feet.}$$

Example 2

Suppose that in Example 1 all conditions remain the same except that the product is in the form of shafts 3 inches in diameter and 42 inches long. These shafts may be heated in a furnace 4 feet wide and loaded on 5-inch centers, or 2.4 shafts per foot of length. The exposed area of each shaft is 2.75 square feet. Then,

$$K = \frac{4 \times 1}{2.75 \times 2.4} = 0.61$$

The mean temperature head is again 300 degrees Fahr., and from Fig. 4 the rate of heating is about 30 pounds per square foot per hour.

Example 3

Suppose that 4500 pounds of steel disks are to be heated per hour from 1000 to 1550 degrees Fahr. (540-845 degrees Cent.) for annealing, which is not so exacting as fine heat treating. The disks are 15 inches in diameter and weigh 15 pounds each, and the exposed area of each is 2.46 square feet. The disks pass in three rows through a furnace 50 inches wide and are loaded on 16-inch centers in the length of the furnace. Then:

$$K = \frac{1.33 \text{ feet} \times 4.17 \text{ feet}}{3 \times 2.46} = 0.75$$

From Table II for preheated stock, the allowable temperature head for fine heat treating is 150 degrees Fahr., and for rough heat-

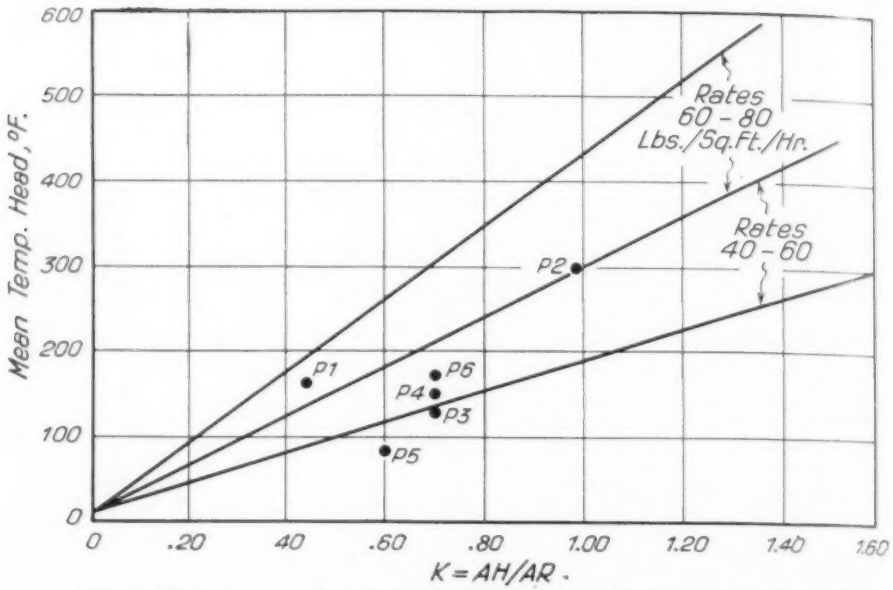


Fig. 5—Curves for a Few Examples of Preheated Stock Showing the Relationship Between Temperature, Rate of Heating and K. See Table I.

ing, 300 degrees Fahr. Selecting an average of 225 degrees Fahr., and referring to Fig. 5 for preheated stock, the allowable rate is 60 pounds per square foot of hearth per hour. The hearth area, then, is

$$\frac{4500}{60} = 75 \text{ square feet.}$$

Fig. 5 has been prepared from the very few examples of preheated stock from Table I, and the lines of the illustration are estimated. The accumulation of additional data will be necessary to establish these lines more definitely.

Conclusion

In conclusion, it must be repeated that the data submitted in this paper are not of sufficient quantity for the determination of absolutely definite relations, although the data available are reasonably consistent. It is the intention to offer an apparently reliable and more satisfactory method of determination of furnace size than has been heretofore available.

DISCUSSION

Written Discussion: By H. C. Barnes, mechanical engineer and furnace designer, American Rolling Mill Co., Middletown, Ohio.

This paper is a valuable contribution to the data on industrial heat transfer, and the range of applications listed in Table I covers most of the common cases of industrial heating. The overall heat transfer coefficient given in this table shows a considerable variation, with a range from 2.4 to 25.8 for cold steel, and is not a constant of general application.

This coefficient is influenced by the fuel used and the type of burners used which determine the luminosity of the flame and its emissivity for radiant heat transfer. The location of the burners will influence this coefficient by their effect on convection. In addition to the area of hearth and exposed area of product, the area of side walls and roof of the furnace have some effect on the heat transfer rate due to reradiation from these surfaces to the product, particularly with clear flames.

The cases listed give some indication of these factors, since the fuel and type of furnace are given, and the individual coefficients given can be used to predict the performance of similar installations doing a similar type of work. The data given are not extensive enough to develop general equations of heat transfer or to supply constants for use in the theory of radiation and convection.

The curves, Figs. 1, 2, and 3, showing the relation between heating rate and overall coefficient or mean temperature head are fairly consistent and may be taken as representative of average practice. The curves, Figs. 4 and 5, showing the relation between the factor, "K" and mean temperature head are rather erratic and indicate that more data are necessary to properly determine the effect of this factor.

Written Discussion: By H. V. Flagg, combustion engineer, American Rolling Mill Co., Middletown, Ohio.

The data on pack heating furnace performance on page 684 were culled from old notes dating back as much as four years. Mean furnace temperatures in most cases were taken as averages of optical pyrometer observations taken over the length of the furnace. Mean temperature product was assumed from the statement:

$$T_m = T_2 - 1/3\ (T_2 - T_1)$$

which gives temperatures somewhat higher than if the logarithmic mean had been employed. Heating surface was calculated as one and one-half times one surface.

The results plotted on curves 1 and 3 do not follow the author's curves, but do indicate a curve slope which is probably characteristic for the peculiar type of furnace and work involved.

Written Discussion: By J. D. Keller, Carnegie Institute of Technology, Pittsburgh.

The writer has been especially interested in the heat transfer coefficients given in the paper.

From the fact that the quantity of heat transferred to the material being heated is equal to the quantity of heat absorbed by it, we have

$$h\ (AR) \cdot \Delta T \cdot t = W \cdot s(T_t - T_1)$$

where h = heat transfer coefficient, (AR) = exposed area of material heated,

Pack Heating Furnaces—Chain Conveyor. Fuel—Raw Producer Gas

Order No.	Product Heated Thin Plate No. Gage, Wdth. Len.	B.T.U. per Pound	Final Control Temp.	Final Temp. Product	Hearth Area Sq. Ft.	Effective Area Product in Furnace One Side x 1.5	$K=\frac{AH}{AR}$	Pounds Per Hour Total		$T_m=T_g-1/3(T_g-T_1)$ Mean Temp.	Heat Rate Lbs./Sq. Ft./Hr.	B.t.u./ Sq. Ft. /Hr./ degree
1	1—0.375—30x41½	240	1750—1650	1510	531	156	3.4	18720	Fce.	1700	35.3	33.3
									Prod.	1050		
									Diff.	650		
2	1—0.205—38½x125	235	1750—1650	1490	531	250	2.13	15170	Fce.	1700	28.6	17.0
									Prod.	1070		
									Diff.	630		
3	2—0.125—50½x68½	225	1700—1600	1450	531	295	1.80	21600	Fce.	1650	40.8	18.7
									Prod.	990		
									Diff.	660		
4	2—0.093—38x62½	238	1630	1530	270	217	1.25	17300	Fce.	1515	64.1	30.0
									Prod.	1040		
									Diff.	475		
5	2—0.125—26½x48½	235	1710	1500	270	131	2.06	10700	Fce.	1690	39.6	21.4
									Prod.	1020		
									Diff.	670		
6	2—0.093—48x44	217	1650	1450	384	228	1.68	11280	Fce.	1525	29.4	15.1
									Prod.	990		
									Diff.	535		
7	2—0.093—48x54½	217	1650	1450	384	255	1.51	14530	Fce.	1525	37.9	17.3
									Prod.	990		
									Diff.	535		
8	2—0.093—48x72	217	1650	1450	384	274	1.40	11370	Fce.	1525	29.6	12.6
									Prod.	990		
									Diff.	535		
9	2—0.125—50½x68½	210		1420	531	288	1.84	21600	Fce.	1620	40.9	18.2
									Prod.	970		
									Diff.	650		
10	2—0.125—66x32	235		1500	384	278	1.34	11720	Fce.	1600	30.5	17.0
									Prod.	1020		
									Diff.	580		
11	2— ? —66x61	210		1420	384	391	.98	13180	Fce.	1575	34.3	9.2
									Prod.	970		
									Diff.	605		
12	2—0.125—50½x53	225		1460	384	317	1.21	12200	Fce.	1580	31.8	11.2
									Prod.	1000		
									Diff.	580		

ΔT = average difference of temperature between furnace and material heated (designated by the author "mean temperature head"), t = heating time, W = weight of material heated, s = its specific heat, T_f = final temperature of material and T_i = initial temperature of material. The equation can be transposed thus:

$$h = s \cdot \frac{(T_f - T_i)}{\Delta T} \cdot \frac{(AH)}{(AR)} \times \frac{W}{(AH) \cdot t}$$

For cases where (1) the objects heated are not of too great thickness, (2) the final temperature of the metal is nearly equal to the furnace temperature, and (3) it is a question of heating-up only, and not of holding at a certain temperature — for such cases the ratio $(T_f - T_i)/\Delta T$ can be considered as a constant, and usually has a value of about 3.3. For iron and steel, the specific heat can be regarded (for the present purpose) as approximately constant, and if the ratio of hearth area to exposed surface of material, AH/AR, were fixed, then we would have

$$h = \text{constant} \times \frac{W}{(AH) \cdot t}, \text{ or}$$

Heat transfer coefficient = a constant × heating rate, lb./sq. ft., hour

which equation, if plotted as in Fig. 1, corresponds to a sloping straight line through the origin. The nearly-straight curve of Fig. 1, therefore, checks well with theory on the basis of the above named assumptions.

However, these assumptions are far from being correct for all of the conditions given in Table I for the various furnaces. Thus, the ratio AH/AR is by no means constant, but varies, according to Table I, from 0.32 to 1.24 (disregarding No. 6, 17 and 25), while the ratio $\frac{(T_f - T_i)}{\Delta T}$ ranges from 1.68 to 8.4, a variation of 5 to 1, the average value of the ratio being 4.0. With such wide variations as these, it is indeed surprising that the points in Fig. 1 fall as close to the average curve as they actually do.

In any case, both ordinate and abscissa in Fig. 1, according to the writer's view, are dependent variables, the independent variables not appearing in this graph. The most important of these independent variables is the temperature. In the attempt to determine some sort of relation, the writer therefore plotted the heat transfer coefficients from Table I against the average of "mean temperature of furnace" (column 14 of table) and "mean temperature of product" (column 15), with the expectation of obtaining a series of curves approximating the form of cubics, the higher curves corresponding to the lower values of AH/AR and vice versa.

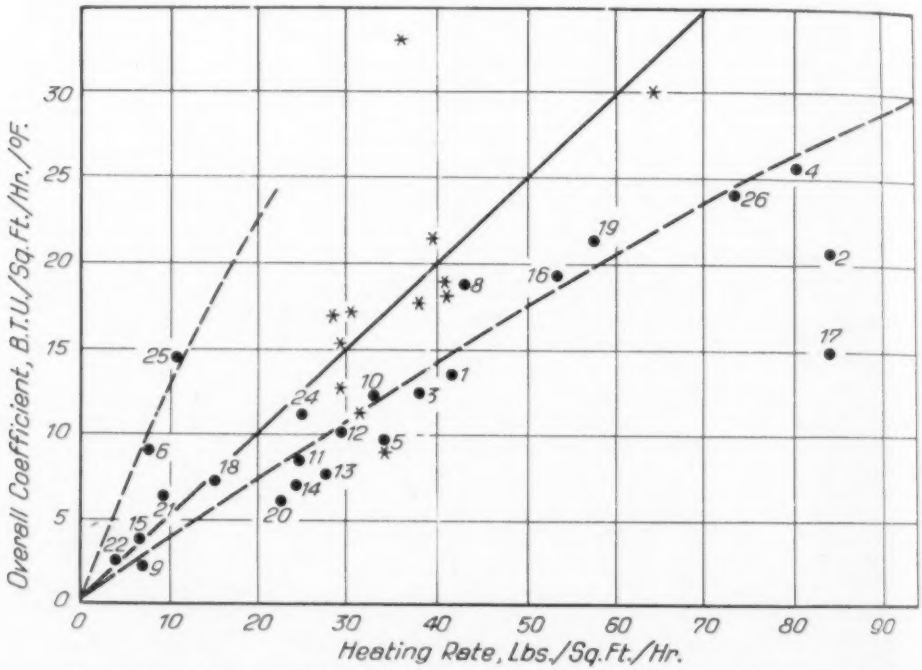
According to elementary radiation theory, the coefficient should vary approximately as the cube of the absolute average temperature. This has been confirmed by G. Wagener, who found that the heat transfer coefficient in his tests when heating steel could be expressed thus:

$$h \text{ (B.t.u. per sq. ft., hr., deg. F.)} = \underset{\text{radiation}}{0.00316 \left(\frac{T_o + 460}{100} \right)^3} + \underset{\text{convection}}{2.05}$$

where T_o = furnace temperature, degrees Fahr. In Wagener's tests, the mean between furnace temperature and average temperature of product was $T_a = 0.85\ T_o$, hence

$$h = 0.00316 \left(\frac{1.18\ T_a + 460}{100} \right)^3 + 2.05$$

When plotted as described, the points from the author's Table I form a band which in a general way follows a cubic curve. As regards the ratio



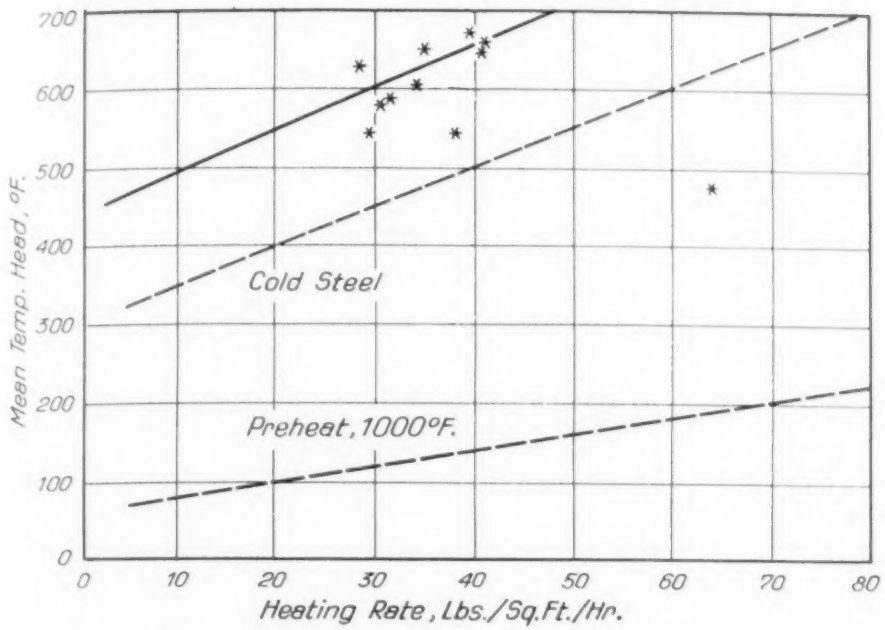
The Above Curves Show Fig. 1 from the Author's Paper (Dash Lines) with that of the Present Discussion Shown as a Solid Line. H. V. Flagg Discussion.

AH/AR, however, no definite relation was discernible, except for a value of the ratio equal to about 0.67, for which the points lay nearly on a curve expressed thus:

$$H = 0.00142 \left(\frac{1.18\ T_a + 460}{100} \right)^3 + 2.05$$

T_a being in degrees Fahr. For other values of AH/AR, the positions of the points were the more erratic, the more extreme the values of the ratio.

The reason for expecting to find a relation between the heat transfer coefficient and the ratio of hearth area to exposed area of stock, is that low values of this ratio should, in general, indicate obstruction of radiation



The Above Curves Show Fig. 3 from the Author's Paper (Dash Lines) with that of the Present Discussion Shown as a Solid Line. H. V. Flagg Discussion.

to some parts of the "exposed surface" of a piece of material being heated, either by adjacent pieces or by parts of the piece itself; while a high value of the ratio should indicate freedom from such obstruction. Thus, for the bowls referred to in the example of calculation of furnace size, where the ratio AH/AR = 0.29, if the bowls are heated open-end-up, the radiation to a point on the inside wall near the bottom is so obstructed by the upper part of the cylinder that it is reduced to only about 13 per cent of the radiation received by a freely exposed surface; and the radiation to some parts of the outside surface is obstructed even more, by adjacent pieces.

On consideration, however, it becomes evident that the ratio AH/AR is only a very rough measure of the obstruction factor or of the "angle factor" for radiation. Furthermore, the coefficient depends upon still another factor, namely, the radiation-absorbing capacity of the surface of the product being heated. Thus, the low values of the coefficient in tests 9 and 22 may well be due to the material having a very smooth surface and correspondingly low emissivity or radiation-absorbing capacity. It is to be wished that experimenters reporting data on heating time or heating capacity would state clearly the nature of the surface of the material being heated, but this is practically never done.

The weak point of the author's method of calculating furnace size appears to lie in the assignment of arbitrary values of the allowable maximum temperature head as in Table II. These appear to have no particular relation to heat transfer requirements; no doubt they are determined almost entirely by metallurgical considerations. The trouble with their use by persons who have not had as much experience as the author, is that they will be applied indis-

criminately in all cases, even those in which the conditions that determined the limits of the values are not present and where, consequently, a smaller furnace could safely be installed, at a saving in cost.

The difficulties in connecting up the figures presented with theory are not to be taken as diminishing the value of the paper; instead, the thanks of furnace engineers are due to Mr. Mawhinney for assembling such a mass of data, especially when the difficulty of obtaining such data on production furnaces is considered. It is to be hoped that Mr. Mawhinney will continue to collect figures on additional furnaces (with, where possible, information as to nature of metal surface, method of supporting the material, arrangement on the hearth, etc.) and will publish them in a future paper.

Written Discussion: By F. J. Ryan, president, R-S Products Corp., Philadelphia.

Without doubt, Mr. Mawhinney has developed some valuable theoretical data in relation to heat transfer, and these data will be valuable in relation to certain restricted classes of heat treating, but it can only be used in a general way in relation to that section of industry where there is a wide variable in the maximum and minimum load charge, and in size and thickness of the material being treated.

Many factors enter into the construction of a fuel-fired furnace which eliminate, in the majority of cases, the use of any ground rule in relation to area of construction. First, let us consider the following:

There is a limit to the minimum of oil input in relation to efficient burner construction. This limit in a gas burner is considerably lower, and therefore it is possible in a gas furnace to install a great many more burners with smaller input than it is oil burners. This condition brings up a variable in heat distribution and circulation, which naturally affects contact, and affects furnace design and the resulting square foot area.

Metal in open position, that is, when not surrounded by other metal and having free access on all sides to the contact of the developed hot gases, has a definite ratio of heat transfer, varying only in relation to temperature of treatment and temperature gradient. When this metal becomes surrounded with other metal and is not spaced in accurate position in relation to each other, which is impossible in the majority of heat treating operations, then there will develop a variable in heat transfer which is not determinable by any equation and must be handled in a general way, preferably by experience.

With the development of automatic temperature control, there entered a new element which affected heat transfer because it reduced oxidation. Oxides are insulators in proportion to their thickness. Probably the most important part of this development lies in the varying condition of venting, which affected furnace pressure, which, in turn, affected heat contact. By this we mean the speed of passage of the hot gases over the work, which again gave a varying condition, which interfered with any accurate method of calculation.

To explain the above, we mean that all furnaces are designed with maximum vent opening. That is, the vent openings are sufficiently large to take off the maximum amount of gases that may be developed for the maximum charge and the maximum speed of heating. Naturally, as the control reaches

temperature it turns off a proportion of the fuel, affecting the proportion of developed hot gases, but with the vents remaining fully open and tending to maintain the velocity of gas exhaust, there is developed a short circuiting in certain sections of the furnace, and if openings around the burners and other sections of the furnace are not sealed, excess air is drawn in. This reduces the temperature gradient during that period or until the gas volume is again turned on to the maximum. This affects the temperature gradient during a definite proportion of the heating cycle and, therefore, eliminates the possibility of relying solely upon calculations.

Our engineering department observing the above conditions spent over three years in accurate study of over 50 different types of furnace equipment of both stationary and continuous types and of both gas- and oil-fired characteristics and they found that it was absolutely necessary to maintain an internal uniform furnace gas pressure in order to set any accurate standard of repeatable operation. It was the result of this study which caused them to tie in through a system of dampers, and centralized vent ports, the variable in the firing cycle as caused by the automatic control in such a way that the vent openings would open and close in accordance with the proportion of the delivered gases.

From our experience, we have of course developed certain standards in relation to furnace areas. These standards vary in accordance with width, height and length, but in any furnace in which there is a varying charge, and a varying type of material being treated, we first determine correct loading area. This allows for efficient ultimate maximum heat penetration without excess heating of the exterior, plus the ability of the work to withstand the pressure of surrounding charge. We then build up the additional area within the furnace to meet the maximum efficiency of heat contact with the lowest possible heat gradient and the most efficient combustion. This all demands the ability of the furnace to deliver the correct proportion of heat both above and below the charge in such a way as to accomplish complete furnace equalization of temperature within a reasonable temperature degree.

These points have been brought out, not with a view of discrediting Mr. Mawhinney's findings, but rather to indicate that while his findings may be correct in relation to a laboratory experiment, that industry is still in the position in relation to heat treatment with fuel-fired furnaces, where it cannot use laboratory calculations for actual determination of furnace areas.

I believe that Mr. Mawhinney's findings are especially valuable in bringing forth the advantage of continuous methods of heat treatment, for with a continuous furnace it is possible to come closer to individual treatment of piece work than it is in a bulk charge furnace. If it were possible to regularly construct furnaces for piece work treatment, then determined factors of area would be extremely valuable, and no doubt there will be an increasing tendency in that direction. However, the general public must realize that you cannot make a race horse out of a truck horse, but rather that each has its place, and consideration should be given as to which is required.

THE HABITS AND LAWS OF DECOMPOSITION OF SUPERCOOLED SOLUTIONS, WITH SPECIAL REGARD TO AUSTENITE

By G. B. Upton

Abstract

The subject really covers a large part of the theory of heat treatment of metals, for most heat treatments start out by forming solutions, solid or liquid, then controlling their decomposition in cooling. β and δ allotropic forms of iron are identical; but α may better be treated as distinct from β, at least as a phase. An example of this is given for the silicon steels; a new equilibrium diagram, keeping α and β distinct, is shown to explain structures and properties of these steels better. Data of supercooling of austenites of all carbon contents under moderate rates of cooling shows temperature "lag" before pearlite, α, or Fe_3C appear to vary about as the cube root of the cooling rate. The "lag" of pearlite is less than that of α or Fe_3C, with the result that the composition of "pearlite" is not fixed, but covers a range of carbon contents, widening both toward iron and carbon as the cooling rate increases. If pearlite has not formed by the time steels cool below 500 degrees Cent., it does not form at all during that cooling; the austenite is supercooled then unchanged to or below the martensite critical temperatures; and martensite forms rapidly. The lag of austenite in supercooling may be considerably controlled by "stabilizing" the austenite in various ways, three of which are described.

The different habits of supercooling for the stable (α, G) as compared with the metastable (α, Fe_3C) eutectoid explain why we almost always get pearlite in handling steels and cast irons. But an analogous case occurs in the freezing of cast irons, where by adding silicon the G eutectic can be made to occur even at high rates of cooling, despite its slow rate of formation, by lifting its freezing temperature well above that of the Fe_3C eutectic, even as supercooled.

Hardened steels contain at least four types of structure intermixed. Untangling of the proportions and prop-

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erties of these four cannot be done by any single set of properties; simultaneous experiments on at least four properties are necessary to solve an equation of four unknowns. This consideration must guide future work in elucidating quantitatively the structures and properties of heat treated steels.

THE whole theory of heat treatment of metals is closely tied with what austenite—the solid solution of carbon in gamma iron—does or might do. We may by analogy study even liquid solutions; and we must study the fields bordering the austenite field. In this bordering region we offer some suggestions that may be novel.

For some time it has been fashionable to deny that alpha, beta and delta forms of pure or nearly pure iron were separate allotropic forms. That is largely a matter of definition; and if the statement of space lattice form and dimensions is accepted as constituting a definition of allotropy, the three are identical. But if the older definition of allotropy stands, that one substance in one state of aggregation (liquid, solid) may have forms differing in physical properties, such different forms being allotropes, then alpha is different from beta and delta, though the latter are identical. Study of any of the equilibrium diagrams of iron alloys having a "gamma-loop," such as that of iron-silicon, will confirm the latter point; the beta and delta fields are one and the same.

Now not only has the old definition of allotropy been challenged, but that of a phase also in an alloy system. A phase is now being defined as a space lattice,[1] a system of sites at which atoms are placed in crystals, further characterized by a ratio between atoms and free electrons in the "unit cell" of the crystal. In this definition there remains no difference between beta and beta prime solid solutions in brasses, near 50 per cent zinc; nor between, we suspect, alpha and beta iron. In both these cases, and similar ones (for they are not few) we maintain that the old definition of physical chemistry, used for the last 50 years, must prevail over the recent suggestion. The old definition of a phase was that it was a mass or entity physically and chemically homogeneous within itself, and different physically and/or chemically from its neighbors. Under this definition alpha and beta iron are separate phases, entitled to their own fields on the equilibrium diagrams; so are beta and beta prime solutions in the brasses separate phases. However, beta and delta solutions in iron

[1]Bragg, Lectures at Cornell University, April, 1934.

alloys are not different phases, but one and the same, as a look at the iron-silicon diagram, for example, will show.

The difference between beta and beta prime solid solutions in the brasses, or between alpha and beta iron, is one of "order" or "disorder" in the arrangement of atoms in the space lattice, or of electrons within or surrounding the atoms. In the brasses the high temperature beta solid solution has the copper and zinc atoms, of about equal numbers, arranged at random in the sites of a body-centered cubic space lattice; the low temperature beta prime solid solution has the same lattice, but the atoms are regularly arranged, in a way that may be described as copper atoms at corners of the cube, zinc atoms at the centers. The transition from one to the other arrangement of atoms, the random and the regular ("disordered" and "ordered"), can be studied mathematically, and described by the intersection of two thermodynamic curves when the arrangement is regular, one curve swinging with regard to the other as temperature changes; but at a certain critical temperature the curves suddenly cease to intersect after having just previously had a common tangency. The onset of the regular arrangement from the random, or vice versa, is thus approached continuously from either side; but there is a discontinuity at the transition. To me the mathematical treatment of the relation of the beta and beta prime phases in brasses constitutes not a showing that they are one and the same, but a very pretty proof that they are different, and a neat showing of how and why they are different.

The change from alpha to beta iron is usually thought of in connection with magnetism. This can be treated exactly as the "order-disorder" of atomic arrangement is analyzed in the beta-beta prime case of the brasses, though now we deal with atom and electron relationships, as is shown by the fact that atoms of iron take magnetism with them into many chemical compounds. Along with the magnetic change many other physical properties, tied with the atom-electron relationships, are different in alpha and beta iron.

Proof that alpha and beta iron may well, or must, be treated as separate phases, because so doing greatly clarifies many of the equilibrium diagrams of alloys of iron, we now give in the case of iron-silicon. Fig. 1 is Stoughton and Greiner's iron-silicon diagram from their American Institute of Mining and Metallurgical Engineers paper.[2]

[2]Stoughton and Greiner, *Transactions*, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1930, p. 160.

The present writer's version of this diagram is given in Fig. 2. The Fe_3Si is dropped entirely, as not called for by any evidence, and contra-indicated by the X-ray findings. We extend their line KG backwards to B, and put in lines FB and AB. Their experiments on electrical resistance versus temperature yield the points along the

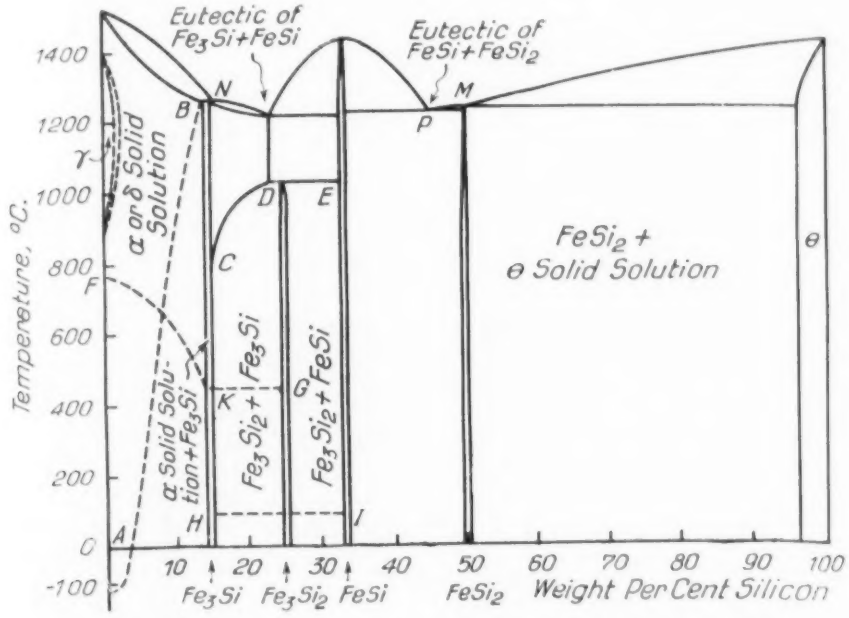


Fig. 1—Stoughton and Greiner Iron-Silicon Diagram (A. I. M. E. 1930).

lines FB and AB indicated by V or Λ. The V points are from heating curves, and indicate that the equilibrium to which they relate should be at a lower temperature; the Λ are from cooling curves. The author's interpretation is that the point K is a eutectoid point of the β (Si) solid solution; the field GKCDG is two-phased, of β (Si) + Fe_3Si_2; the field FBKF is two-phased of α (Si) + β (Si); the field FBA is single-phased, of α (Si).

α (Si), β (Si), and Fe_3Si_2 (?) are all body-centered cubics, very similar in dimensions; this meets the X-ray data. Fe_3Si_2 is formed by a peritectic reaction at D at 1020 degrees Cent. (1870 degrees Fahr.), from β (Si) and FeSi; but this change is slow and usually incomplete. Hence Fe_3Si_2 is hard to locate by microscope or X-ray, and the magnetic change of β (Si) to α (Si), at 450 degrees Cent. (840 degrees Fahr.), may be traced at times between the composition of Fe_3Si_2 and FeSi. From β (Si) or α (Si), at temperatures 450 degrees Cent. (840 degrees Fahr.) or lower, Fe_3Si_2 precipi-

tates along BKG or AB like Mg_2Si in duralumin, but even quenching is not a fast enough cooling to stop this precipitation, which gives immediate "age hardening" and brittleness. The effect of annealing below ABKG is to soften, and raise the ductility, by aggregating the Fe_3Si_2. Pilling's data on brittleness of iron-silicon alloys have two

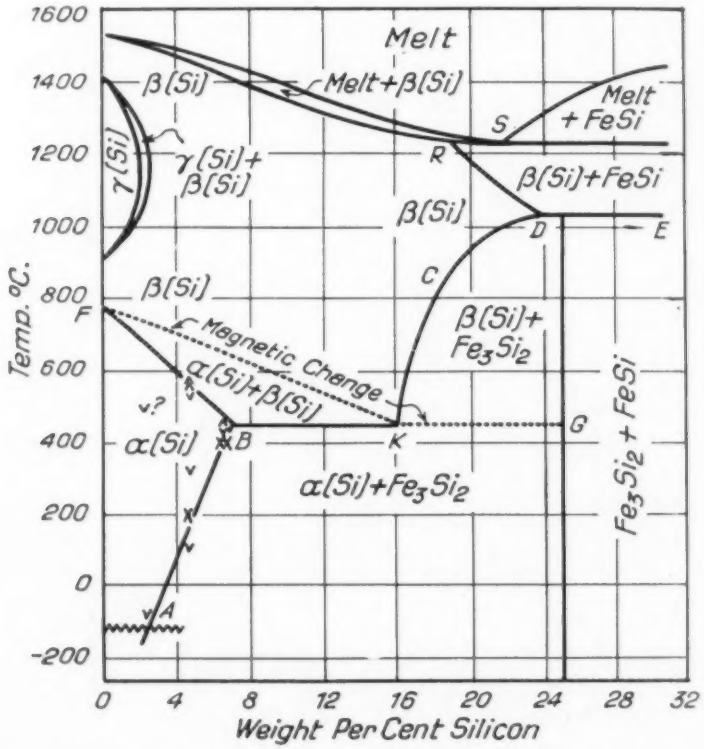


Fig. 2—Upton Diagram of First Part of Iron-Silicon System.

causes: the precipitation hardening just mentioned, below AB, and crossing that, a bit below —100 degrees Cent., and indicated by a jagged line, the general cold-brittleness that comes to most iron alloys at low temperatures. The writer does not believe that the line AB swings sharply to the left just below the point A. Within the α (Si) field, and above —100 degrees Cent., the alloys are ductile.

I submit that as soon as we admit that α (Si) and β (Si) can be and are different phases, we get the iron-silicon diagram in the form of this Fig. 2, clearing up in a consistent whole all the microscopic and X-ray structure, the physical and engineering properties of the silicon steels. Similar diagrams are feasible and useful for all the alloys giving "gamma-loops."

For the description of the behavior of austenite we may discuss

first the experiments of T. Sato.[3] Sato worked with a series of over a dozen nearly pure iron-carbon alloys, covering the carbon range to 1.55 per cent. These steels he heated and cooled through the critical temperatures at various rates of change of temperature, observing the structural changes by magnetometer and dilatometer.

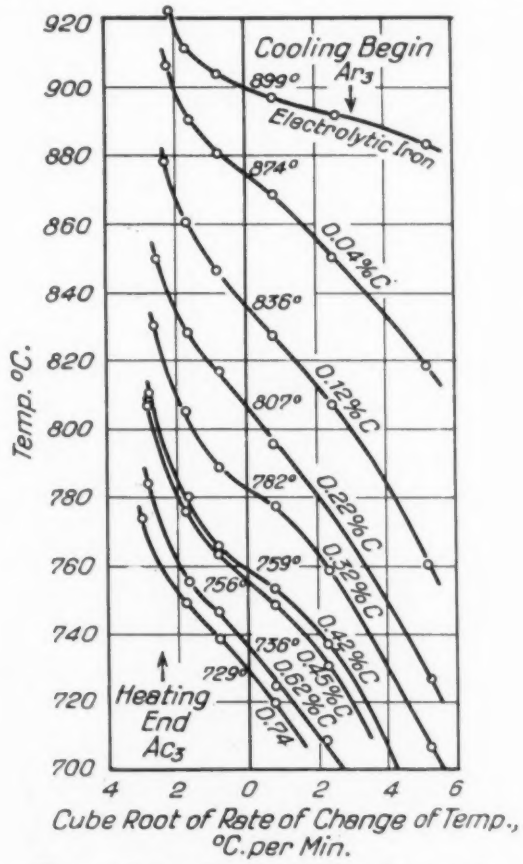


Fig. 3—Sato's Data of Supercooling and Superheating, Hypoeutectoids.

He plotted the beginnings (or endings) of Ar and Ac points versus rate of change of temperature, obtaining parabolic looking curves tangent to the axis of zero rate of change of temperature at the equilibrium temperature. These tangencies are very difficult to estimate with satisfaction. After trials of various relations, the present author found that the superheating or supercooling "lag" of a critical point is quite nearly proportional to the cube root of the rate of change of temperature. In Figs. 3, 4 and 5 are shown Sato's data replotted as temperature versus the cube root of the rate of change of tem-

[3] "On Critical Points of Pure Carbon Steels," Technology Reports of Tohoku Imperial University, 1928.

perature, putting heating data on one side of the axis of zero rate of change of temperature, cooling data on the other side. The equilibrium temperature is then where the common curve from the heating and cooling sides cuts this axis of zero rate of change of tempera-

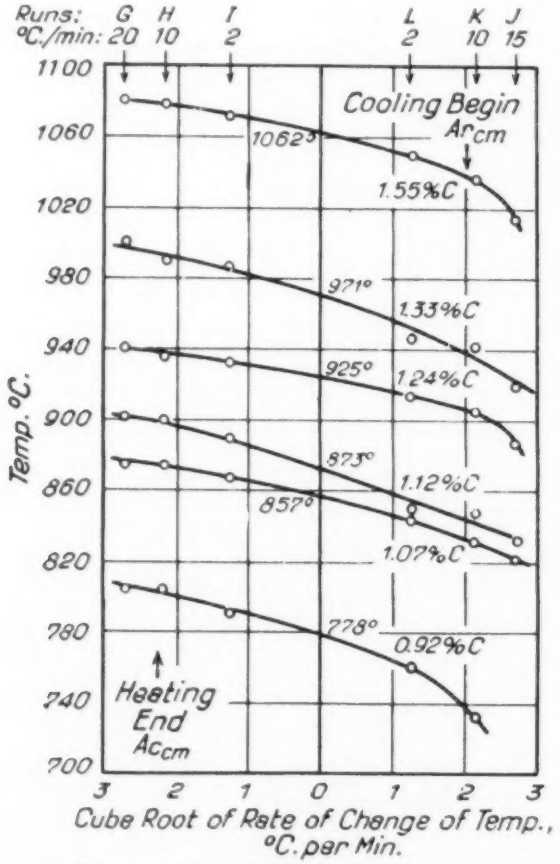


Fig. 4—Sato's Data of Supercooling and Superheating, Hypereutectoids.

ture, and is now very satisfactorily found. The wildness of some points on these curves is probably due to rate of change of temperature not being quite as reported; the detailed reporting of Sato's data is unsatisfactory in this regard. In Fig. 6 is shown the equilibrium diagram of iron-carbon (for Fe_3C system) as recovered from the Sato data. Note the straightness of the Fe_3C saturation line, the pearlite composition at 0.78 per cent carbon, and the distinctly different lines of separation of beta and alpha iron from austenite.[4]

[4]Compare the substantially equal diagram obtained by another method from Sato's data by Yay, Chu-Phay, TRANSACTIONS, American Society for Steel Treating, March, 1933. Mr. Yap's method has not the merit of bringing the equilibrium temperature in the middle of the plot, as in Figs. 3, 4, 5 here.

Sato's cooling rates covered the range from 0.5 degrees Cent. per minute to 150 degrees Cent. per minute. The slopes of the curves in Figs. 3, 4 and 5 give equations for the supercooling "lag" of beginning of precipitation of beta, alpha, Fe_3C, or pearlite from austenite, in the empirical form supercooling = constant times the

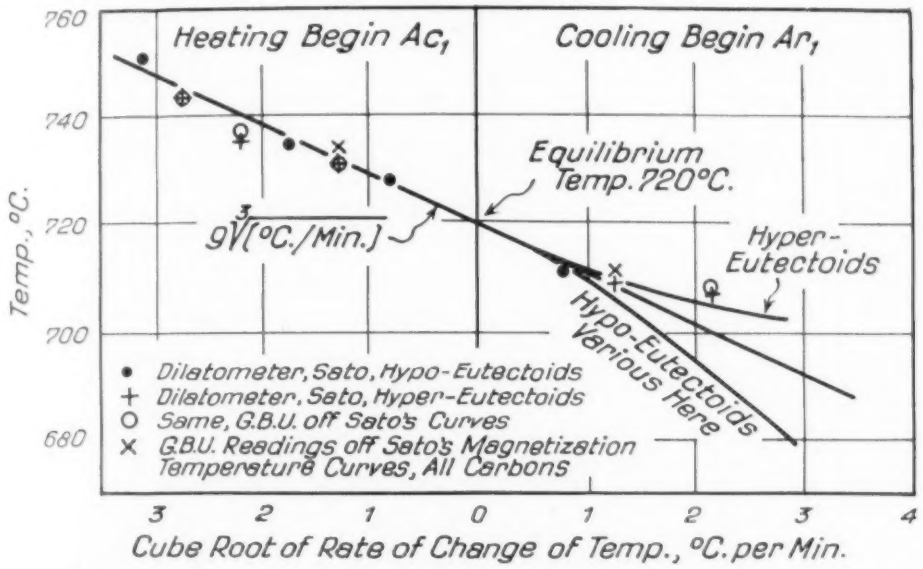


Fig. 5—Sato's Data; Critical Temperature, Superheating and Supercooling of Pearlite.

cube root of the rate of cooling in degrees Cent. per minute. I find no change of these supercooling lag constants with composition of the austenite, except for pearlite below 0.4 per cent carbon. For beta and alpha iron the constant comes out 12+; for Fe_3C 13; for pearlite 9 (except for carbon contents below 0.4 per cent, where the constant increases). It is not surprising that beta and alpha should act alike; but it is rather surprising that Fe_3C should have the same lag as beta or alpha. Most remarkable is the lesser lag for pearlite as compared to its components alpha and Fe_3C individually. The consequences of this are shown in Fig. 7. The upper solid lines of this Fig. are the equilibrium diagram lines of the bottom of the austenite field. The parallel sets beneath are the lines of beginning of precipitation from supercooled austenite of beta, alpha, P (pearlite), or Fe_3C, for a number of successively increasing rates of cooling. Note that as a consequence of the lesser supercooling of pearlite than of its components the composition of pearlite is a point only at equilibrium; at any finite rate of cooling, that is, in any practical case, pearlite has a range of composi-

tions from where its lesser supercooling eats up the end of the alpha line on one side to where it eats the end of the Fe_3C line on the other side. The cooling rates shown in Fig. 7 go far beyond Sato's range, and the extrapolation may not be safe numerically, but in principle it should be safe. The faster the cooling rate, the wider

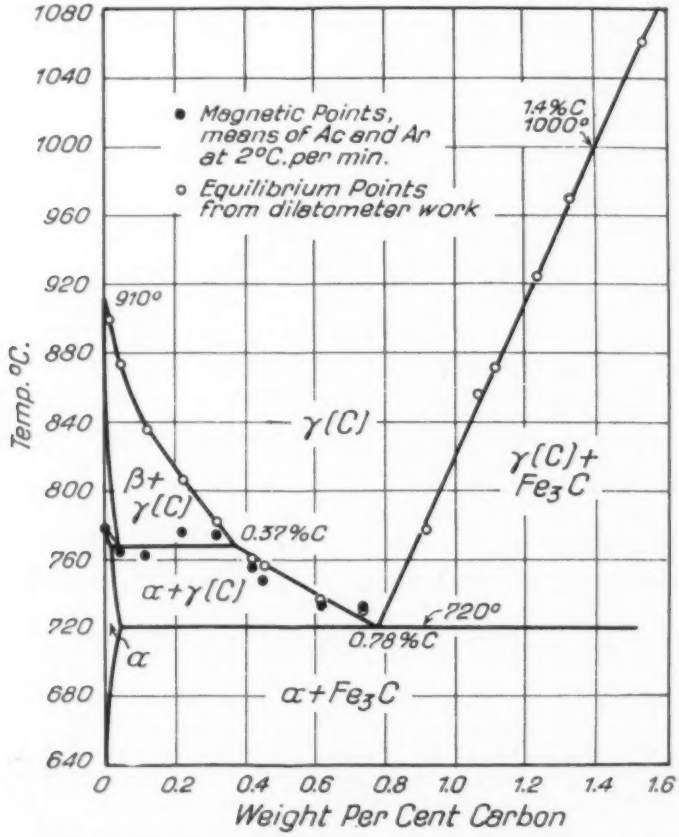


Fig. 6—Fe-Fe_3C Equilibrium, Drawn by Upton from Sato's Data.

is the range of composition of pearlite, particularly on the low carbon side of the equilibrium eutectoid. We are all familiar in practice with the increase of pearlite area in a cross section and decrease of ferrite, in a medium carbon steel cooled at increasing rates; but the author believes that this is the first theoretical explanation of that familiar phenomenon. Note that at the cooling speeds of water quenching pearlite would extend well over toward pure iron; or in other words, the difference in equilibrium temperatures between iron and pearlite precipitations from austenite would be wiped out by the difference between supercooling lags. Again, we have known that on cooling curves $Ar_{2,3}$ and Ar_1 points

merged as cooling rates increased, but have not usually recognized that such merging resulted in such a showing as Fig. 7. The final consequence is that at high cooling rates, as in heat treatment quenching, we need look only for the pearlite precipitation out of the

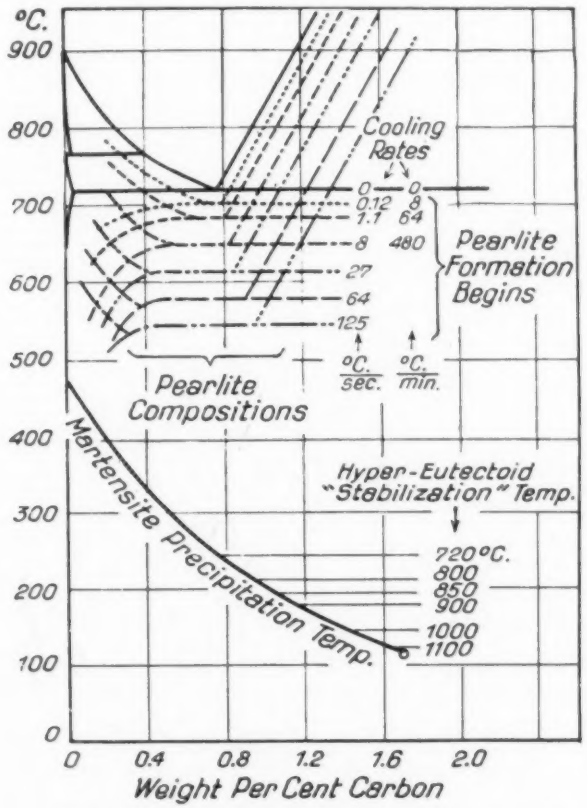


Fig. 7—Composition and Precipitation Temperatures of Decomposition Products of Austenite (Pearlite and Martensite) at Various Cooling Rates, and After Various Stabilizations.

austenite, for the alpha and Fe_3C precipitations will be merged in that; and such pearlite will have the composition of the austenite, not eutectoid composition.

While we are studying Fig. 7, we may see in its lower part the critical temperatures at which martensite precipitation begins during cooling in carbon steels. These temperatures are of a reaction in supercooled austenite, and the temperature depends on the amount and nature of the alloy in solid solution in the austenite; in this case practically carbon only. Inspection of the curves of Davenport and Bain[5] shows that at 550 degrees Cent. (1020 de-

[5] *Transactions*, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1930.

grees Fahr.) carbon steels require 0.5 to 1.0 seconds to start pearlite formation, and 5 to 10 seconds to complete it. Below 500 degrees Cent. (930 degrees Fahr.) these required times increase with great rapidity as the temperature falls. Hence it is entirely safe to say that, during a continuous cooling of a steel, if the pearlite change

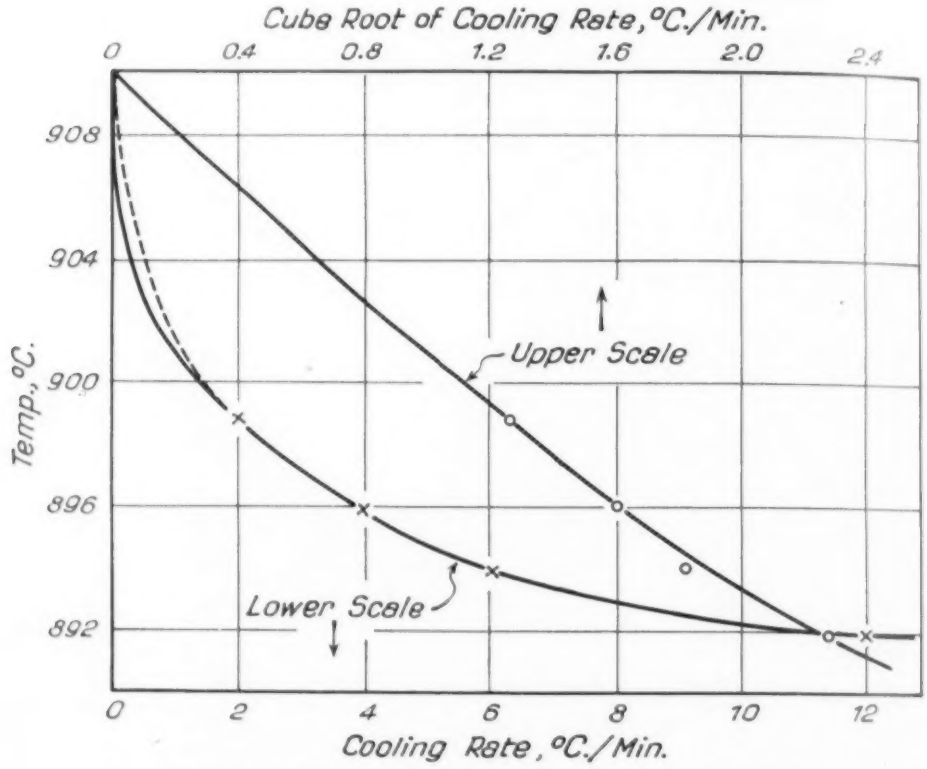


Fig. 8—Data of Ruer and Klesper on Supercooling in "Pure" Iron.

has not occurred before the steel passes 500 degrees Cent., that change is suppressed and the austenite supercools to and below the martensite critical temperatures. The martensite formation becomes rapid within 50 degrees Cent. drop below the martensite critical temperatures. It does not follow by logic, but it seems plausible to expect, by downward extension of the way the composition of pearlite spreads out as its temperature of formation lowers, that martensite would have the composition of its preceding austenite. This is now generally admitted to be the case.

In Fig. 8 we have applied the empirical law of supercooling varying with cube root of cooling rate to data of Ruer and Klesper[6]

[6]*Ferrum*, 1914.

taken from National Metals Handbook. The original authors, plotting the data versus first power of the cooling rate, getting a parabolic curve tangent to the temperature axis, guessed 906 degrees Cent. (1663 degrees Fahr.) as the equilibrium transition temperature of $\gamma \rightleftarrows \beta$ change. Fig. 8 shows it should have been about 910 degrees Cent. (1670 degrees Fahr.). The slope in Fig. 8 is 8+ when cooling rate is in degrees Cent. per minute; Sato's steels gave 12+, except that for electrolytic iron he had 3+. Here we find the *form* of the empirical law is general, but the *constant* is variable as we change the source or preparation of the sample.

The variation of the supercooling lag constant with source and preparation of sample is one aspect of the familiar phenomenon known in heat treatment practice as "stabilization" of the austenite. "Stabilized" austenite is slower to react in cooling than unstabilized; in the present language of this paper, it has a greater constant of supercooling lag. There are three actions concerned in stabilization. Due to superheating lag, analogous to supercooling lag, we have to heat a steel considerably over the equilibrium lower boundaries of the austenite field before it becomes entirely austenitic; i.e., loses all vestiges of the low temperature forms α, P, Fe_3C. But when γ (c) is first fully formed it is not internally homogeneous as to composition. To make it homogeneous requires time for diffusion of iron and/or carbon back and forth—half an hour to even several hours of holding at constant temperature. If we do not give diffusion time the parts low or high in carbon in the austenite form nuclei of alpha or Fe_3C earlier on cooling than would be the case if we had given time for diffusion to equilibrium—the unhomogeneous austenite reacts faster than homogeneous austenite. Quite inseparable in practice from the effect of departure from homogeneity is the factor of grain size (or crystal size) of the austenite. The boundaries of a crystal are usually and inherently more active than its core when changes are starting (except when nonhomogeneity is great); hence the finer the austenite grain size the faster does it react on cooling. Reaction rate is perhaps proportional to number of grains per cubic inch.[7] Lastly, and particularly in tool steels and alloy steels (whenever we are dealing with the right hand boundary of the austenite field, the saturation lines for carbon or for other alloying elements) we can change the com-

[7]Deduced from data of Bain, Campbell Memorial Lecture, TRANSACTIONS, American Society for Steel Treating, 1932.

position of the solid solution austenite by choice of the holding temperature for stabilizing the austenite. By increasing the content of the austenite solid solution as to carbon, vanadium, manganese, nickel, chromium, tungsten, etc., we can markedly slow up the reaction rate of that austenite when we cool it; and in many cases we also change the critical temperatures at which such stabilized high-alloy austenite reacts in cooling—notably the martensite point which depends mainly, as the pearlite point does not, on the composition of the austenite. See the bottom part of Fig. 7 for this effect of stabilizing temperature on martensite critical temperature, and for carbon as alloying element.

We now follow out the consequences of the supercooling lag laws into wider fields. The iron-carbon system has two alternative equilibria, the Fe-Fe_3C and Fe-G systems. The Fe-G system is the more stable, the slower to form; it is a generality of chemical reactions that the metastables are faster than the stable reactions where both are possible. A. E. White, some years ago,[8] stated that when malleable iron is being made the pearlite eutectoid occurs on cooling if the cooling rate exceeds 5 degrees Cent. per hour; the Fe-G eutectoid occurs only when the cooling rate is less than 4 degrees Cent. per hour. The temperature separation of the two eutectoids is here perhaps 10 degrees Cent., the Fe-G at the higher temperature. Obviously, the supercooling lags of the two eutectoids are so related to each other that up to cooling rates of 4 degrees Cent. per hour the G eutectoid occurs first; above 5 degrees Cent. per hour the Fe_3C eutectoid occurs first. With Sato's supercooling lag constant for pearlite the supercooling of that eutectoid at 5 degrees Cent. per hour cooling rate is about 4 degrees Cent. At this same cooling rate the stable Fe-G eutectoid must be supercooled 10+4 = 14 degrees Cent.; hence its supercooling lag constant must be of the order of 3.5 times as great as that for pearlite. The relations of the two eutectoids are shown in Fig. 9a. As soon as the cooling rate is great enough to bring the supercooled G eutectoid temperature close to the (less) supercooled Fe_3C eutectoid, the more rapid action of the latter will dominate. Since we almost never cool steels, even in furnace cooling, at rates slow enough (less than 2 degrees Cent. per hour) to give the G eutectoid a chance, we practically never see any but the pearlite eutectoid.

The probable scheme of action of cast irons at the eutectic

[8] TRANSACTIONS, American Society for Steel Treating, 1926, p. 214.

(freezing) temperatures, and possible scheme at the eutectoid temperatures, is seen in Fig. 9b. Silicon raises the equilibrium temperature of the G eutectic considerably (15 degrees Cent. for each weight per cent Si) and has practically no effect on the temperature of the Fe_3C eutectic. The separation of the two eutectics, at

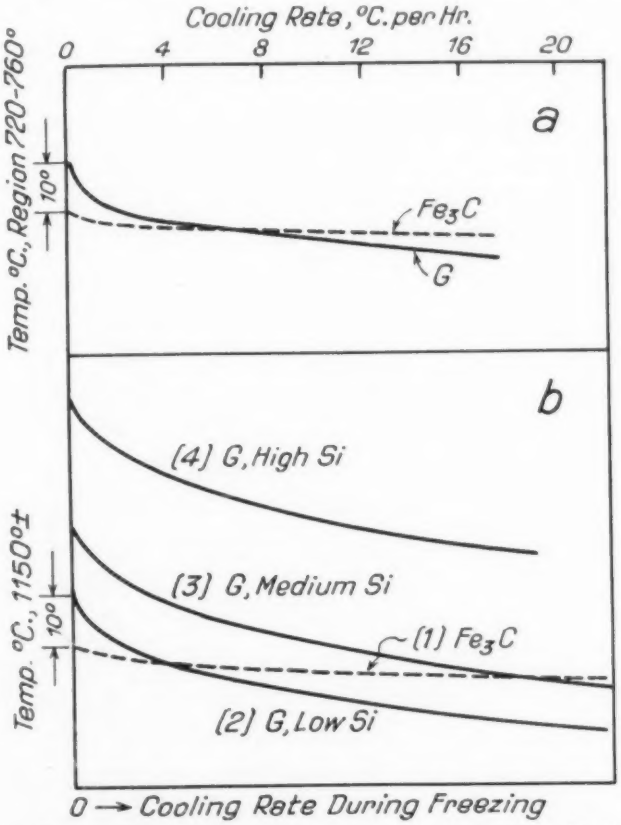


Fig. 9—Relations of Stable Fe-G and Unstable Fe-Fe_3C Systems at Eutectoids (a) and Eutectics (b).

equilibrium, is not over 10 degrees Cent. at low silicons, but increases relatively sharply as silicon rises. Curve (1) in Fig. 9b represents the temperature of beginning of Fe_3C eutectic versus cooling rate for all silicons; curve (2) the corresponding G eutectic at low silicon; (3) the G eutectic at medium silicon; (4) the G eutectic at high silicon. Obviously, at low silicon we will ordinarily get the Fe_3C eutectic, at medium silicon we will ordinarily get the G eutectic, but by chilling (very rapid cooling) we can get the Fe_3C eutectic and with high silicon we cannot make white cast iron even with fairly drastic chill. Added to relations shown in Fig. 9b one other factor nearly completes the statement of basic

relations of gray and white cast irons to each other at freezing. This other factor is the latent heat of freezing, which rises with either carbon or silicon increase. When the latent heat is high it becomes difficult to force rapid cooling during the eutectic freezing. The laws of supercooling of solutions then explain the relations of white and gray cast irons. "Mottled" cast irons are of course those where the cooling rate is such that the two eutectics are both forming simultaneously during the freezing, at comparable rates.

The statement of an approximate empirical law of supercooling, and showing of its power to explain much in heat treatment relations in steels and cast irons, is not a stopping point of our study if we can make more detailed analysis of what lies behind the empirical approximation. This deeper analysis is now becoming possible. Some of the Germans are already attempting analyses of the laws of chemical reactions in the solid. We have in this country, in the Davenport and Bain paper on "Transformation of Austenite at Subcritical Temperatures,"[9] when we back that up with other papers in world literature of metallography of the last ten years or so, a fairly adequate basis for beginning of a quantitative analysis of heat treatment reactions, which are simply chemical reactions in solid crystalline material, occuring over a far wider range of temperatures than a chemist usually has had to deal with. The law of supercooling, with which we have been dealing, is but one small part of this wider field now opening up before us.

Davenport and Bain, in the paper just mentioned, worked with five kinds of carbon steels, one low alloy and one high alloy chromium steel. Numerous samples of each steel were heated in the lower part of their austenite fields, as for heat treatment hardening, and then suddenly transferred to quenching baths thermostatically controlled. The bath temperatures covered in many steps the region from room temperature to the pearlite critical, A_1, of each steel. After various lengths of stay in the quenching bath, from seconds to months, specimens were withdrawn, water-quenched, and examined microscopically for amount and kind of change undergone. At some lower temperatures a dilatometer was clamped onto the specimen as it went into the quenching bath and kept on to record dimensional changes versus time. Results were plotted with temperatures of quenching bath as ordinates, with contour lines of logarithms of time to certain decimal amounts of change of

[9] *Transactions*, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1930.

austenite toward its final steady condition at the bath temperature used. One of their figures is reproduced here as Fig. 10.

A survey of all of their figures for carbon contents 0.5 to 1.2, confirms the spread of composition of pearlite with increasing super-

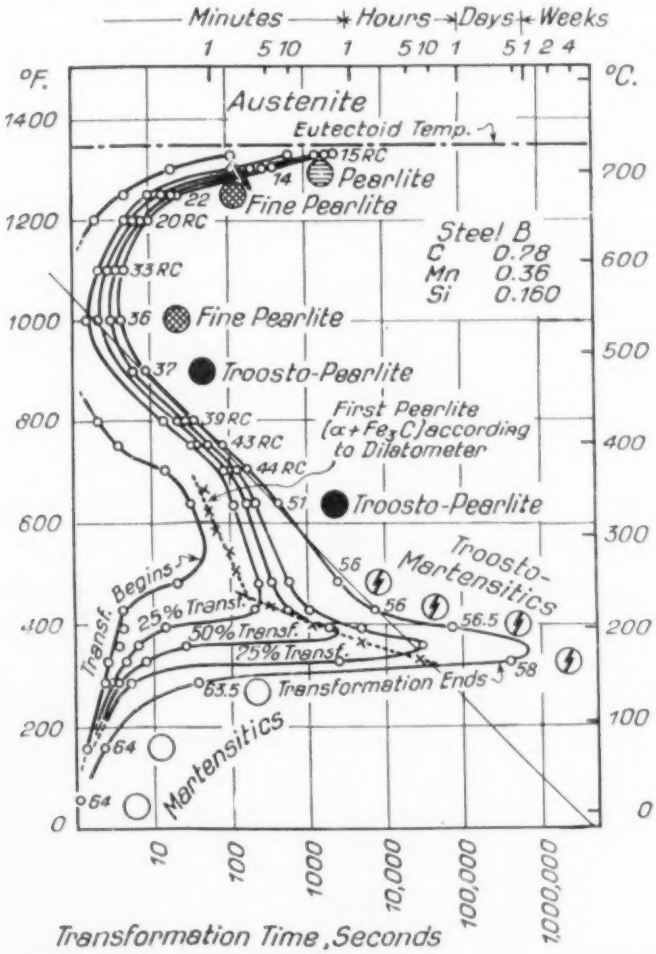


Fig. 10—Decomposition of Austenite at Constant Temperature, at Various Temperature Levels under the A_1 Critical Temperature (Davenport and Bain With Additions by Author).

cooling as shown in Fig. 7, but with less spread toward alpha and more toward Fe_3C than there indicated. They noticed little or no proeutectoid carbide even with carbon at 1.13 and 1.17 per cent. The cause of this most probably is that proeutectoid carbide must be large in amount to be observed as such, that small amounts may be lost in pearlite.

One feature of Davenport and Bain's charts of log-time for various percentages of transformation versus temperature catches

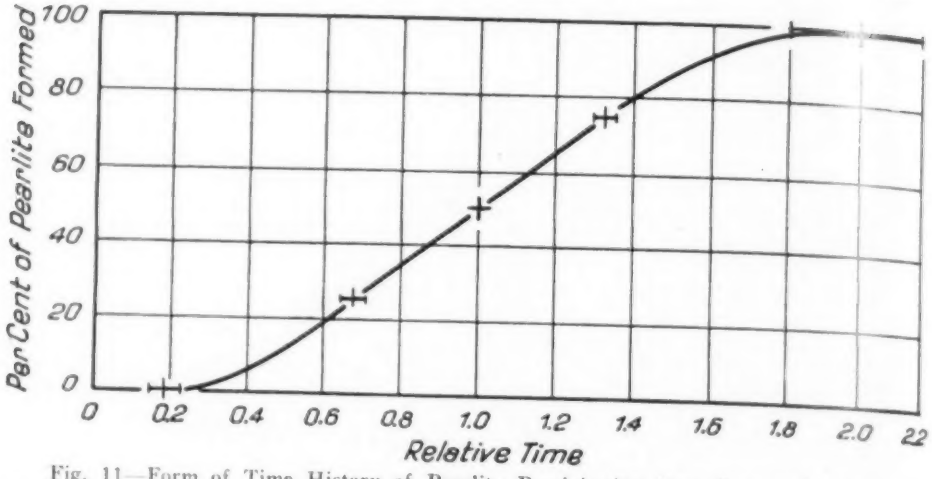


Fig. 11—Form of Time History of Pearlite Precipitation from Supercooled Austenite, at All Temperatures Where it Occurs.

the eye immediately. It is that the contour lines for equal percentages of formation of pearlite are parallel over the temperature range from the pearlite critical temperature to the martensite critical temperature. That is to say, the relative internal history of pearlite formation is the same over all this temperature range; the only change is in the time scale of time required. Hence it is possible and permissible to average the log-time versus per cent change data for all temperatures in the range mentioned to find for each steel the typical form of the pearlite transformation versus time. The numerical results of this averaging are shown in Table I, and plotted in Fig. 11.

Table I

Steel	Composition, Weight Per Cent				Critical Temperature °C		°F		Relative Reaction Time for Percentage of Formation of Pearlite				
	C	Mn	Si	Cr	P	M	P	M	0.5	25	50	75	99.5
A	1.13	0.30	0.17	0	728	190	1345	375	0.19	0.71	1.00	1.32	2.00
B	0.78	0.36	0.16	0	728	250	1345	480	0.15	0.67	1.00	1.32	1.85
C	0.54	0.46	0.20	0	728	300	1345	570	0.21	0.70	1.00	1.39	2.24
D	0.50	0.91	0.13	0	724	285	1335	550	0.32	0.74	1.00	1.53	2.56
E	0.64	1.13	0.09	0	724	260	1335	505	0.16	0.65	1.00	1.31	2.30
F	1.17	0.30	0.18	0.26	735	170	1355	340	0.28	0.74	1.00	1.31	2.04
G	0.38	...	...	13.	815	240	1495	470	0.13	0.63	1.00	1.25	1.53
					Average without D				0.19	0.68	1.00	1.32	1.99

The relative times have been averaged for all the steels except D, because that one seems to have mislaid its 50 per cent time relative to its other times. Fig. 11 plots these average results as the type of relative reaction time at constant temperature for various structural percentages of pearlite to be formed from austenite.

The effect of different temperatures, used as the temperature locus for this pearlite formation, is simply to change the actual amount of time corresponding to the unit of time in Fig. 11. Unit time is taken at the 50 per cent change point because in that region the times can be much more accurately fixed than at the 0.5 and 99.5 per cent points, where the curve is too flat for accurate time measurement. The mean time deviations from the averages are indicated in Fig. 11, the unity at 50 per cent change having been forced.

It will be noted in Fig. 10 that this formation of pearlite is all that the steels do between the pearlite critical temperature and the martensite critical temperature. The only effect of temperature change in that interval is to change the time required for the pearlite formation. As temperature falls this time comes down from infinity at Ae_1 to a few seconds at around 1000 degrees Fahr. (540 degrees Cent.); then lengthens rapidly as temperature falls further. Nevertheless, we have not been calling all the results of this pearlite reaction pearlite. Below the temperature of minimum time of reaction, or maximum rate of reaction, the product has commonly been called "nodular troostite." It grows more or less spherically from a few nuclei which are commonly found along crystal boundaries of austenite. Inside each nodule we now know, from the work of Lucas and of Davenport and Bain, the structure is that of pearlite, simply much smaller in crystal size than the pearlite formed at higher temperatures. There are two other structures in steels also called troostite. One of these is a ternary eutectoid of alpha iron, iron carbide, and alloy carbide, forming at about 400 degrees Cent. (750 degrees Fahr.) in such low alloy steels as 3.5 per cent nickel, 1.7 per cent chromium.[19] This ternary eutectoid may form in addition to a regular pearlite in such steels; because of the low temperature of formation it is nodular. The third troostite is the first product of decomposition of martensite in tempering. The author ventures to suggest that the first two kinds of "troostite" ought to be called "troosto-pearlite," to make clear at once their appearance and their real nature; while the last one only might properly be called troostite. It might also be added that the presence of Fe_3C in the real troostite is quite dubious. Its specific volume and electric resistance are both higher than for sorbite, into which troostite goes by further tempering; and both excess specific volume and excess electric resistance of

[19] Andrew, Rippon, Miller and Wragg, *Journal*, Iron and Steel Institute., 1920, I.

troostite over sorbite, plotted against carbon content, give straight lines joining with the sorbite properties at zero carbon, showing that alpha iron is present in both alike, but the carbon condition is different. Further, magnetism (flux density in strong field) decreases at over 200 degrees Cent. temperature when troostite is tempered to sorbite, corresponding to using up of hitherto alpha iron in forming of carbide, which at those temperatures is non-magnetic.[11]

Now consider the variation of rate of formation of pearlite with temperature between the pearlite and martensite critical temperatures. There are two temperature factors involved. One is the effect of absolute temperature on all chemical reactions, making them slower as temperature falls. The other varies with the temperature drop below the critical temperature, and tends to make the reaction faster as the temperature drop increases. The interaction of the two temperature effects gives the minimum of reaction time noted for pearlite formation at around 1000 degrees Fahr. (540 degrees Cent.). We will try to untangle the two effects, which we may call Φ (T) and Ψ (T_c-T). The Ψ (T_c-T) may be peculiar to this reaction, though its type is general; the Φ (T) is a general function.

In text books of physical chemistry one finds that time rate of reaction, over wide ranges of temperatures, is given by the form

$$\log R = -\frac{A}{T} + B + CT,$$

where R is reaction rate, A, B, C are constants. For lower temperatures the CT term is commonly omitted; but for high temperatures it becomes, in the end, the dominant term of the expression. Searching for some convenient way to show how this equation works out, the writer has picked, as perhaps the easiest to visualize, the plotting against absolute temperature of the size of the increment of temperature required to double reaction rate. Differentiating the expression for reaction rate with regard to temperature, and remembering that $\log_e 2 = 0.693$, one gets the increment of T to double reaction rate $= \triangle T = 0.693T^2/(A+CT^2)$. At low temperatures this gives $\triangle T$ varying as T^2, for CT^2 is negligible; but at high temperatures the expression approaches 0.693/C, a constant. Hence the form of the relation of $\triangle T$ to T is as shown in Fig. 12.

[11] Matsushita and Nagasawa, *Journal*, Iron and Steel Institute, 1927, II.

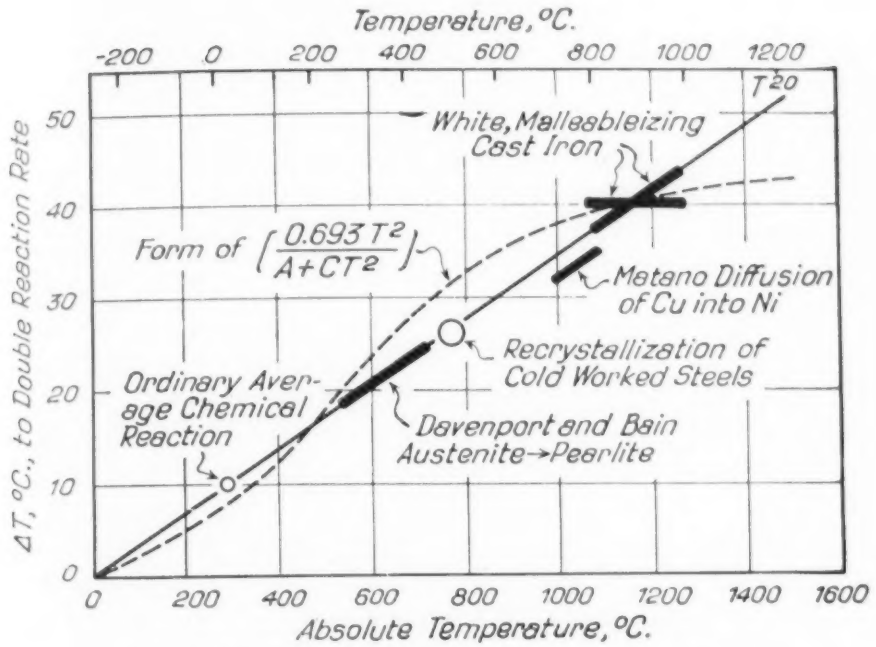


Fig. 12—General Effect of Temperature on Reaction Rates.

On this Fig. we spot a few things we know, as that at room temperature chemical reactions commonly double in rate for about a $\triangle$T of 10 degrees Cent.; at about 500 degrees Cent. $\triangle$T to double rate of recrystallization of cold-worked steel is 25 degrees Cent.; in malleableizing cast iron $\triangle$T is 40 degrees Cent., at temperatures 1500 to 1900 degrees Fahr. (820 to 1040 degrees Cent.).

We need to be careful as to what and why we choose for values of this $\triangle$T. In general, reactions in the solid require atoms to move from here to there, to get together with their new partners and build the new crystals. Hence, basically, reaction velocities in the solid are conditioned by diffusion velocities. $\triangle$T is controlled not by the absolute value of diffusion velocities but by the effect of temperature on relative increase of those velocities. Take for example the recent work of R. Schneidewind and A. E. White on malleableizing.[12] As soon as Fe_3C begins to break down, it forms γ (c) between the G and the Fe_3C, and the solid solution thenceforth transfers carbon atoms from decomposing Fe_3C to the G particle which is growing. The driving force is the greater solubility of carbon from Fe_3C than from G in the γ (c); the speed of diffusion depends on the distances between nuclei. Plots of reaction time against

[12]University of Michigan Engineering Research Bulletin, August, 1933.

temperature in the Bulletin give 40 degrees Cent. = $\triangle T$ to double reaction rate; but they fit equally well the twentieth power of absolute temperature when reaction time is plotted logarithmically versus absolute temperature. A survey of Fig. 12 raises question whether $\triangle T$ should be represented by an S shaped curve, or by a straight line through the origin. If $R = mT^n$, then $\triangle T = 0.693T/n$, a straight line through the origin with slope $0.693/n$. Since it seems likely that pearlite formation rate depends on diffusion through austenite just as malleableizing does, we have plotted Davenport and Bain's curves of log-time versus temperature in the form of log-time versus log-temperature; and find that beginning a bit below the temperature of minimum time, and down to the temperature of martensite formation, the slope of the log-log plot is about 20 for their steels A to F inclusive; G is not available. Hence we feel it justified for the present at least to use the approximation $\Phi(T) = mT^{20}$, for it appears valid from 300 to 550 degrees Cent., and again from 800 to 1050 degrees Cent., and can hardly fail to be valid between those two ranges and also fairly well outside of them.

Multiplying the times of reaction for various steels for pearlite formation at various temperatures by T^{+20} leaves two parts, a constant specific to the reaction, and the function $\Psi(T_c - T)$. The results are shown for the different steels in Fig. 13, as $\log_{10}$ [constant x Ψ $(T_c - T)$] versus $(T_c - T)$. The hyperbolic form of these curves suggests strongly that log $\Psi(T_c - T)$ approaches zero or a very small value as $(T_c - T)$ increases. There is no point in trying to push this analysis of $\Phi(T)$ and $\Psi(T_c - T)$ much further, for each depends on the other here, and independent accurate knowledge of $\Phi(T)$ is needed before $\Psi(T_c - T)$ can be really evaluated.

The general form of the $\Phi(T)$ and $\Psi(T_c - T)$ functions is well enough shown, however, to form the basis of an important argument. It seems incredible, in view of the forms of these functions, that $\Psi(T_c - T)$ should suddenly throw a fit, so to speak, at the martensite critical temperature, so that martensite could be explained as a sudden, vastly more rapid, precipitation of $\alpha + Fe_3C$ (troosto-pearlite). Yet such an explanation of the Ar″ critical temperature of steels has often been offered. Using the $\Phi(T) = T^{20}$ to approximate the effect of absolute temperature, to make comparison of the minimum times of formation, of martensite with those

of pearlite, as of the same temperature, it comes out from the Davenport and Bain data that martensite formation has a reaction rate from a billion to a trillion times as fast as pearlite; the jump required in $\log_{10} \Psi(T_c - T)$ is 9 to 12.

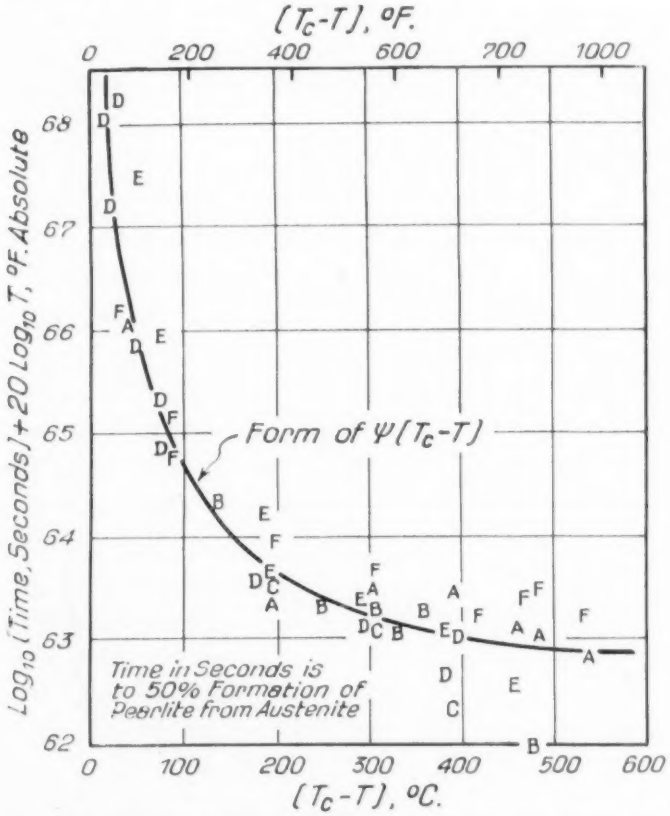


Fig. 13—Form of the Function Ψ (T_c-T) the Effect of Distance Below its Equilibrium Critical Temperature on Time Rate of a Reaction.

The X-ray shows martensite to contain a tetragonal form of iron, not the cubic alpha; the electrical resistance is as high as that of gamma iron, not low like alpha; the specific volume is 3 per cent or more greater than alpha, agreeing with the X-ray data for the tetragonal iron; magnetism increases when martensite tempers to troostite, corresponding to the change of tetragonal iron to cubic alpha, and indicating that tetragonal iron (real martensite) is non-magnetic. Iron carbide can be looked for by its characteristic reversible loss of magnetism between 150 and 200 degrees Cent.; martensite and troostite do not show this, but sorbite does. The implication here that Fe_3C is not present in martensite and troostite cannot be dodged by argument about submicroscopic size of the

carbide; all the evidence about relation of size of carbide to magnetic properties shows it more strongly magnetic as its crystal size decreases; as if, perhaps, the carbide had absorbed alpha iron on its surfaces. Do not assume that a statement that tetragonal iron (real martensite) is probably nonmagnetic means that martensitic steels are nonmagnetic; the maximum amount of tetragonal iron is probably never over 35 per cent of the whole, and most of the rest is alpha except for carbon contents toward 1.5 and fairly drastic quenches from very high temperatures.

Other very convincing evidence that martensite formation cannot be a suddenly revivified, enormously speeded pearlite reaction is found in the steels of nickel 3.5 per cent, chromium 1.7 per cent.[13] These can be stabilized to show, in the same specimen in one single cooling, pearlite at 600 degrees Cent., ternary eutectoid at 400 degrees Cent., and martensite at 150 degrees Cent. Since in one specimen in one cooling pearlite cannot be both supercooled to 150 degrees Cent. and not supercooled below 600 degrees Cent., this experimental showing entirely wrecks the theory that martensite is the same as pearlite, but forming rapidly at a low temperature when stopped at a high one. Yet martensite must be an iron phase, for the critical temperatures of martensite formation shown in Fig. 7 slope down with increasing carbon just as do the beta and alpha lines below the γ (c) field above. Martensite has its own $\Psi(T_c - T)$, its own critical temperatures, independent of alpha iron. That martensite is tetragonal iron, an unstable allotrope, if you wish, different from alpha iron, seems an inescapable conclusion. Whether the carbon in martensite is in solid solution can be answered only by the final settlement, now in doubt, whether the space lattice shown by the X-ray changes with increase of carbon content.

We return now to another Fig. of the Davenport and Bain paper, reproduced here as Fig. 14, showing hardness of *completed* transformation products for the different quenching bath temperatures. Note that there is no jump in hardness when martensite comes in; simply a progressive increase of hardness in going from pearlite to fine pearlite to troosto-pearlite to troosto-martensitic to martensitic. In the range above the martensite critical temperatures there is no question that increasing hardness is due to increasing smallness of average crystal size. Is it not then reasonable, in view of the continuity of these hardness curves against temperature of

[13]Andrew, Rippon, Miller, and Wragg, *Journal*, Iron and Steel Institute, 1920, I.

structural change, to say that in the martensitic structures also the hardness is due to still finer average crystal size? In this connection we have plotted elsewhere data of hardness of alpha brass versus number of crystals per linear inch, a presentation which plots substantially a straight line; extrapolation of that line to the number of crystals per inch indicated by X-rays for martensite would predict brass of that crystal fineness to have Brinell 3000! There

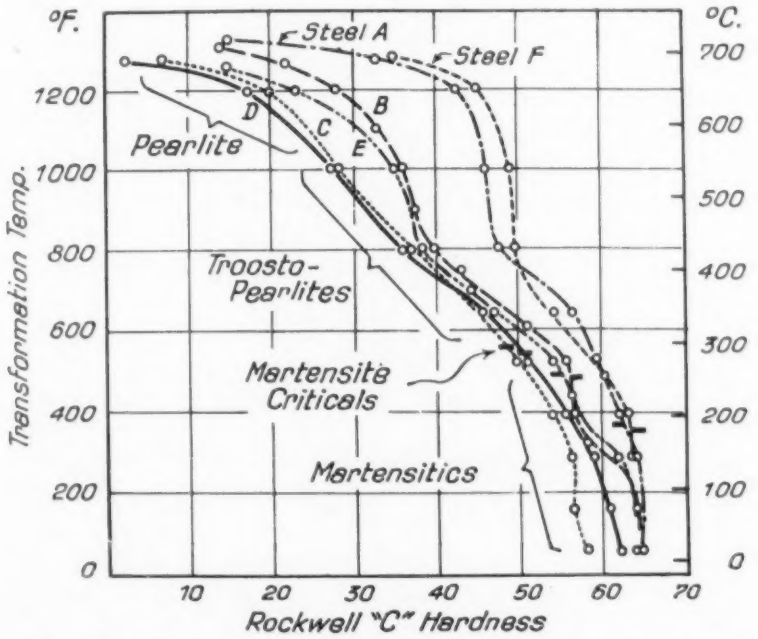


Fig. 14—Davenport and Bain's Figure of Hardness of Completed Transformation Products of Constant Temperature Transformations of Austenite, with the Author's Marking of Martensite Critical Temperatures of Each Steel Added to Their Figure.

is no need to call upon any factor but crystal size to account for the hardness of hardened steels.

In Fig. 15 are reproduced the dilatometer curves of Davenport and Bain for their steel B, the same steel to which Fig. 10 applies. Note in the upper part of Fig. 10 the pearlite formation, of form as given in Fig. 11. Then, in the lower part of Fig. 15, note the very different habit of formation of martensite. Pearlite has a considerable time lag before any pearlite shows; martensite forms immediately and most rapidly at the start. In form of transformation amount versus time, martensite has the form which a physical chemist would call the mass law form for a first order reaction. If A represents austenite, M martensite amounts, the shape of

the martensite transformation curve corresponds mathematically to such a scheme $dA/dt = -RA$ at constant temperature; $dM = -dA$. There is no time lag for martensite as there is for pearlite; consequently, as experiment indicates, martensite formation cannot be supercooled.

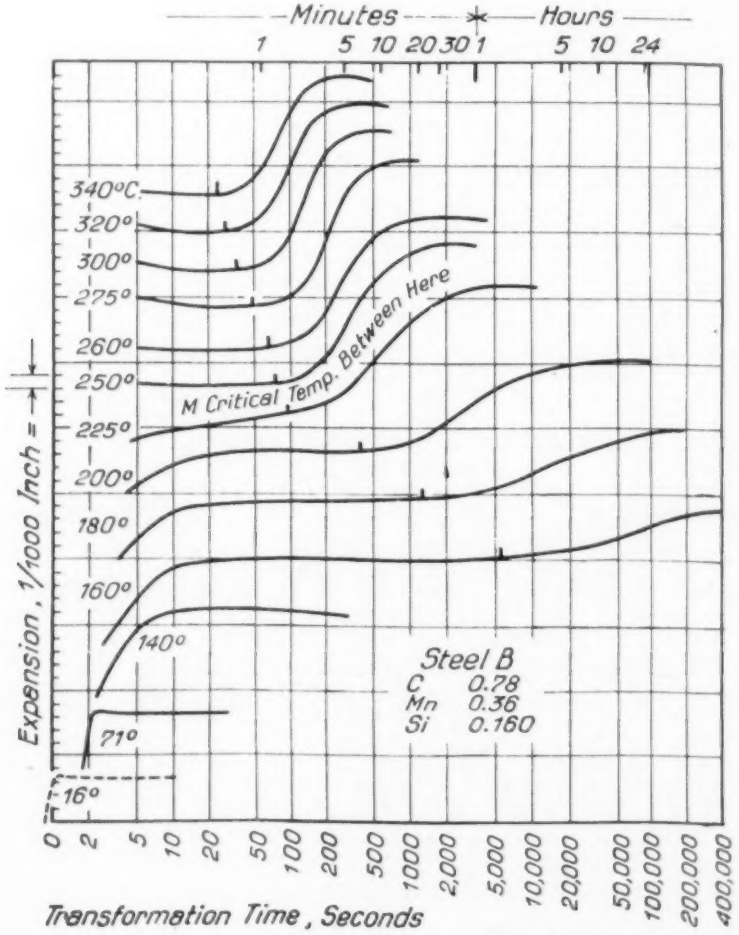


Fig. 15—Dilatometer Curves of Transformation of Austenite at Constant Temperatures. Davenport and Bain Figure with Additions by Author as to Martensite Critical Temperature and Beginning of Pearlite.

Pearlite formation has that time lag at the start which makes supercooling possible. All solution decompositions which can be supercooled, whether of liquid or solid solutions, must be of the pearlite type.* They appear to belong to what the chemist calls

*The textual argument following is correct if reactions in the solid follow the kinetics of reactions in gases or liquids. But conceivably reactions in the solid require (a) a time rate of formation of nuclei, (b) a time rate of growth upon the nuclei, complicated by mutual interferences of such growths. This would make a story of reaction mathematically quite different from that in gas. See discussion by Dr. Mehl.

sequential or chain reactions. In this case, austenite changes to X_1, this in turn to X_2, this in turn to pearlite; I do not intend here to say just how many intermediate, unknown or unrecognized stages there must be between austenite and pearlite, but there must be one and may be two or three. Sato's experiments with dilatometer and magnetometer make it clear that up to the first appearance of pearlite in supercooled austenite the austenite does not reveal what is going on within it, as X stages, which is to produce pearlite as an end product.

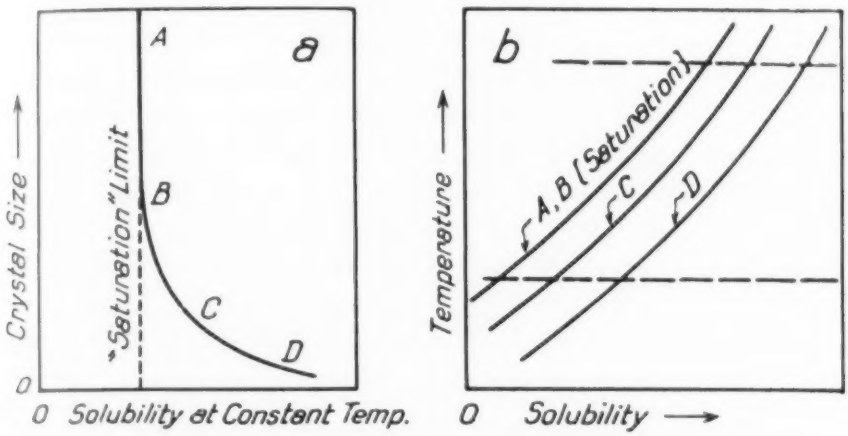


Fig. 16—Solubility Relationships as Affected by Crystal Size.

One part of the X stages in the chain which ends in pearlite is the formation of nuclei in the austenite, of things about to be from decomposition of the austenite. This nucleus formation tangles up in the variation of solubility which is a function of crystal size, as shown in Fig. 16a, and 16b. In Fig. 16a solubility at constant temperature is plotted against crystal size, in the curve ABCD. For large crystals, at A or B, solubility is fairly fixed, and this solubility of large crystals is what we know commonly as the "saturation" limit for the solution. But when crystals are made smaller they are found to be more soluble as their size decreases, as at C and D. This determination is a common enough experiment in chemistry, but we do not know where the curve goes to when the crystal size becomes submicroscopic, below D. The principle involved comes into the growth of crystals; if both large and small ones are in contact with a common solvent, the small ones will dissolve and the dissolved material precipitates out on the large ones, making them grow at the expense of the small ones. We are familiar with such growth of crystals in metals reheated after working. An-

other aspect of this variation of solubility with crystal size is shown in Fig. 16b. The ordinary saturation line is AB, for larger crystals. Smaller crystals have each a solubility line appropriate to their size, like C and D. The letters in Fig. 16a and Fig. 16b correspond to each other, A in one to A in the other, etc.

Now apply the solubility-crystal size relationship to nucleus formation in a supercooled solution, which means one cooled below its saturation line. We may view austenite as a solution of alpha iron and carbon in gamma iron. The kinetic heat motions of atoms in the space lattice may result in change of electron structure of gamma atoms to make temporary alpha atoms; other chance motions may release carbon atoms from solution. But such release cannot last at small supercoolings, for the released material is smaller than D while the solubility conditions are in the region near AB, Fig. 16b; the too small stuff released will re-dissolve. Not only must atoms of alpha and/or carbon be released, but big enough groups of such atoms be formed and released so their size will be greater than the solubility limit size corresponding to the temperature at which they are released. Hence at temperatures below but near the saturation line nuclei are few, large, and slow to form; at a lower temperature nuclei are more numerous, smaller, quicker to form. This accounts for the $\Psi(T_c - T)$ function which quickens precipitations from the supercooled solutions as the temperature level drops. Then comes in the general effect of absolute temperature in slowing up heat motions of heat atoms, and slowing diffusion; ultimately perhaps decreasing the number of nuclei forming.

After nuclei of alpha iron and carbon have been formed as a start toward pearlite, reaction must take place between the carbon and some form of iron to make Fe_3C. The formation of Fe_3C is faster than the growth of graphite. The formation of alpha iron from gamma requires considerable movement of iron atoms from their positions in the gamma space lattice. In nucleus formation, carbide formation, and growth of crystals of alpha and Fe_3C, we may have found enough X stages to make up the chain of reactions in pearlite formation. The more intermediate steps there are in such a chain, the later in the total reaction time do the first signs of the final product appear; and the time history of pearlite formation, as shown in Fig. 11, has so late a start of pearlite showing as to indicate at least two intermediate stages.

Martensite (tetragonal iron) formation from gamma iron re-

quires very little atom motion to take up the new configuration. Hence it can be a fast action even at low temperatures. The octahedral planes of densest packing of iron atoms in austenite are also natural planes of similar packing in the tetragonal iron, so that growth of martensite along such planes is very easy and quick. Hence the structure of martensites. And hence also its refusal to supercool; its lack of delay stages of chain reactions.

Martensite has a trick of action which is peculiar to reactions in the solid involving considerable volume changes. At low temperatures austenite is 2.5 to 3 per cent more dense than the pearlite condition of the same steel, but martensite is 3 per cent less dense—a density or volume jump from austenite to martensite of 5.5 to 6 per cent, an expansion when martensite forms. In a liquid or a gas pressures must be hydrostatically equal throughout the mass during a chemical reaction, except with detonations; but in a rigid solid great local, point to point almost, variations of pressure are possible. A compression stress will stop martensite formation from austenite, stabilize the austenite. Hence martensite formation, as is well known, behaves differently during cooling of a piece of metal and during holding at a steady low temperature. At steady temperature the martensite formation is self-stopping by local pressure effects. In contact with forming martensite the austenite will be under compression, but at a distance other austenite must be under tension to bring about the general balance of tension-compression stresses through the piece as a whole. This tends to make a banded intermix of martensite and austenite layers, with a spacing fixed by the stress variations. It is this banded intermix of austenite, martensite, and probably troostite which is commonly called martensite. Further, during a sustained cooling the outside of a piece, being cooler than the inside, tries to shrink more, and so the outside goes into tension, the inside into compression. The severity of these stresses depends on size and shape of piece. Their general effect is to promote martensite formation in the outside parts, and inhibit it in the inside.

Instead, then, of a simple mass law statement of the formation of martensite as a first order reaction, in the form $dM = -dA$, and $dA/dt = -RA$, where M = amount of martensite, A = amount of austenite, we must put $dA/dt = -R(A - bM \pm C)$. Recognizing that the amount of A, residual, equals $(A_o - M)$, where A_o is the original amount of austenite at time zero, we get $dM/dt =$

$R(A_o - M - bM \pm C)$. The term bM recognizes the local pressure increase to be proportional to the amount of martensite formed; the term $\pm$ C represents the regional pressures due to continued cooling. At steady temperature the term $\pm$ C vanishes. Integration gives

$$M = \left(\frac{A_o \pm C}{1 + b}\right) \left(1 - e^{-(1+b)Rt}\right).$$

The final martensite is $\left(\frac{A_o \pm C}{1 + b}\right)$; the retained austenite is $\left(\frac{bA_o \mp C}{1 + b}\right)$. We would not want to argue that these equations hold clear to the end of the action, but they characterize its beginning and give the nature if not the exact values of the final results. Mathematically, the factor (1+b) becomes a scaling factor on both the ordinate and abscissa of the curve of M versus t of martensite formation; the final amount of martensite formed is less than without the pressure effect in the ratio 1/(1+b); and the time to finish the reaction, or to reach a given relative stage of reaction, is less in the ratio 1/1+b). And in proportion as formation of martensite is stopped, austenite is retained. Here we see why, also, oil and water quenches differ, through the operation of the factor $\pm$ C of regional pressures; and why continued cooling bringing in the factor $\pm$C, gives a different result than steady temperature.

Pressure effects can occur to reactions in the solid whenever volume changes accompany the reaction and the elastic limit and moduli of elasticity are high enough to permit the pressures to build up. The volume change austenite to pearlite is only half that of martensite formation, but when the martensite critical temperature is low enough, the immediately preceding pearlite formation can show also an austenite stabilization and retention. This happened in one of Davenport and Bain's steels.

Pressure effects are also important in the tempering of hardened steels, making the changes during heating up in the tempering bath much more rapid than the continuing changes after a piece comes to temperature in the bath—quite a time-saving scheme for practical heat treatment. Time in the tempering bath becomes important chiefly for relief of cooling stresses.

Hardened steels contain more or less of many structures—austenite, pearlite or sorbite, martensite, troostite, to name the four groupings which have fairly definite sets of properties. To find out how much a steel contains of each of these requires measurement simultaneously of at least four sets of properties—four unknowns require four equations to fix them. Until, then, systematic experiments are done wherein many samples of one steel are put through many heat treatments and stages of treatment, and at each stage at least four critical properties of the metal are measured simultaneously, we cannot solve the problem of the amounts of the various structures in the steel and the contributions of each to the final results. Such research work in heat treatment theory and practice remains to be done. We have made a start.

DISCUSSION

Written Discussion: By H. A. Schwartz, manager of research, National Malleable and Steel Casting Co., Cleveland.

A discussion of so generalized a paper as Upton's must of necessity be limited to certain "high spots" which happen to attract the attention and interest of the commentator.

The question of whether alpha and beta iron are, or are not, two distinct phases has become, in the writer's mind, purely a matter of definition. If entities are to be separable from one another there must be some criterion by which they differ and since magnetism furnishes such a criterion there appears reason to consider them as distinct phases. On the other hand, the concept of phases and components arose out of the Gibbs investigations on heterogeneous equilibria. The conclusions which are now embodied in the Phase Rule imply a difference in free energy content between two phases of the same substance. From this viewpoint the coexistence of two phases in a one component system is impossible over a temperature range at constant pressure. The usual assumptions as to the character of the magnetic change near A_2 are then not in accord with the concept of a distinction of phase. When we contemplate the possibility of the existence of two forms of a pure substance differing in some detectable property but not in energy content, ambiguity is unavoidable. The fact that A_2 is not depressed by solutes points to a small difference at most of free energy level between the magnetic and nonmagnetic states.

In doubtful cases the present writer happens to prefer an interpretation in the light of the phase rule to any other, feeling it more consistent to leave that unaltered at the expense of redefining a phase rather than the reverse.

It appears that in Figs. 3 and 4 the author has not actually adhered to his cube root relation, for he draws a smooth curve through the observational values and not a straight line as he would have done had he had unbounded confidence in the cubic function. Drawing a smooth but empiric curve through points plotted as a function of the cube root of the rate of change of

temperature with time yields no information not furnished by a similar curve in which the cooling or heating rate rather than its cube root is used as the abscissa. Either curve would intersect the line of zero cooling (or heating) rate at the same point. It may be suggested that the author would have more consistently adhered to his own thesis had he represented these plots by the best straight line which might be drawn through them.

The explanation of the occurrence of the stable or metastable systems during the cooling of iron-carbon alloys, substantiating the so-called Stufenregel of Tammann by calculation of the point at which a eutectic, or eutectoid, should form as a function of cooling rate is, to the present writer, the most interesting part of the paper. This interest is not materially decreased even if the cube root relationship should ultimately not be completely substantiated.

Written Discussion: By R. F. Mehl, director, Metals Research Laboratories, professor of metallurgy, Carnegie Institute of Technology, Pittsburgh.

There is no subject that can be presented to a metallurgical audience more powerful in producing discussion than that of the decomposition of austenite. As a matter of fact the great wealth of information that is now available on the subject and the very many scientific aspects of the problem make it a bit difficult to restrict a discussion of the general phases of the subject within any reasonable scope. This paper by Professor Upton is extremely thought-provoking. It has, as you may see, two major sections, the first concerning the nature of the α-β change in iron and the second, which is the main topic of the paper, on the decomposition of austenite. The discussion I have prepared concerns chiefly the second, but before entering into this part, I should like to comment briefly on the first part.

The way in which Professor Upton has drawn the Fe-Si diagram is very ingenious. I believe, however, there is little scientific justification for it. Evidently much of the argument must depend upon the point of view adopted considering the α-β change in iron. Whether this should be regarded as a true allotropic change or not is of course an argument which has grown hoary with age in metallurgical circles and about which there can still exist two classes of opinion. I am among the group which sees little reason for considering the change as a phase change. Let me illustrate by listing the arguments on this side of the question. The α-β change in iron is one which is shown by the change in the magnetization, the α phase losing its ferromagnetism on heating at the A_2 point. Accompanying this change there is also a change in heat content, for heat absorption is noted. This reaction, however, is a curious one. It is characterized by no change in density, by no change in a_o, the side of the unit body-centered cubic cell. There is no change in microstructure and accordingly there can be, and is, no possibility of altering the structure of iron or steel by heat treatment involving the use of the A_2 point. This change differs from other changes which are known to be true phase changes in a number of very important respects. The magnetism is not lost at constant temperature. It is lost over a range of temperatures beginning at a relatively low temperature and extending up to 800 degrees Cent. The accompanying heat change is likewise distributed over a range of temperature of about 20 degrees Cent. reaching a maximum at a point where the magnetization curve has the greatest slope.

I shall show these data on the board drawn from experiments conducted in my laboratory by Dr. Walters. The change further differs in the fact that it shows no hysteresis. The A_2 point for a given sample of iron is at the same temperature for the rates of cooling varying from 15 to 250 degrees Cent. per minute heating or cooling. Evidently therefore we are not dealing with a heterogeneous reaction where one phase changes into another, for such reactions must take place at a constant temperature and must by the nature of heterogenous reactions be characterized by hysteresis, that is, must be characterized by a time rate of change. Both of these factors are of importance in arguments which are intended to lead to an adoption of points of view concerning the nature of the A_2 point. We may also characterize a true allotropic change by the behavior of the thermodynamic potential or free energy curves. Each phase will have its own thermodynamic potential or free energy curve, and these curves will not intersect over a range of temperature but at a particular temperature. This is perhaps as close a definition of the meaning of phase as we can attempt, and in view of the characteristics of the α-β transformation this transformation cannot be classed among true phase changes.

Accordingly, therefore, it should not be permissible to combine a curve of magnetic change with curves of true phase changes upon a constitutional diagram as shown in Fig. 2. We may argue the point somewhat obliquely by stating that no satisfactory combination of this sort has ever proved useful in the study of metal systems, but I should prefer to argue it more directly, namely, that the thermodynamic principles governing phase changes are well understood and unique; whereas no ordinary thermodynamic treatments can be advanced for governing the changes in magnetism, which are purely intra-atomic.

The iron-silicon system is, to be sure, a complicated one, and there remains a great deal to be done in studying the behavior of this system in its relationship to constitution. Many of the peculiarities come from the well known brittle constituent present in electrical sheet. This constituent is, however, a carbide and is therefore an impurity in the iron-silicon system. The peculiar behavior of the lattice dimensions in the range up to 20 per cent silicon, as shown by Phragmén and later by Jette, is at the moment entirely unexplained. Incidentally both these workers find that the side of the unit cube varies progressively through the field which in Fig. 2 is marked as a heterogeneous field. This would not be the case were the field truly heterogeneous. Heterogeneity is characterized at a constant temperature by unchanging values of the lattice parameters of the constituent phases throughout a heterogeneous field. Although the combination shown in Fig. 2 seems to simplify the constitution of iron-silicon alloys, I am inclined to believe that it is an oversimplification and scientifically not justifiable.

I might note that there is considerable justification for the definition of a phase as a unit cell which Professor Upton calls into question in the last paragraph on page 691 and at the top of page 692. A unit cell, of course, is not a concept but a physical entity determined directly by X-ray diffraction. The unit cell will distinguish between what Professor Upton calls order and disorder in the arrangement of atoms in a space lattice. For those beta solid solutions which are body-centered cubic the unit cell of the disordered lattice is simply

an ordinary body-centered unit cell, but for the ordered lattice it is designated a lattice with a super-structure. The unit cell is again body-centered cubic but of the caesium chloride type in which the body-centered cubic cell is obtained by the interpenetration of two simple cubic lattices, one composed of one sort of atoms and one composed of another. Accordingly the specification caesium chloride type gives a unit cell, different in this way from that when the specification is body-centered cubic alone.

Besides the general interest attached to Professor Upton's discussion of the decomposition of austenite which I believe to be quite new in many respects and to be very valuable, I find the discussion interesting because it is directly related with work which is going on at the moment in my own laboratory. The treatment of the results of Sato shown in Figs. 3, 4, and 5 is very interesting. I wonder if Professor Upton has any explanation of the importance of the cube root of the cooling or heating rates and straightening out of the critical points found. The method he uses, however, is a very convenient graphical method of evaluating true equilibrium temperatures even though the meaning of the cube root may not immediately be apparent. Sato's data are quite good data. It must be pointed out, however, that Sato's alloys were not especially pure, and I believe probably somewhat irregular with respect to purity. You will note from Sato's data that the silicon content occasionally was sufficiently high to account for a rather appreciable increase in the $A_{3.2}$ temperatures. According to Sato's analyses the percentage of silicon varies around an average of 0.10 per cent, lower in the hypoeutectoid alloys and higher in the hypereutectoid.

The method of preparing the steel is, as Professor Upton suggests, of great importance in determining the amount of undercooling which the alloy will exhibit and will therefore determine the curves shown in Fig. 7. Incidentally this treatment given in Fig. 7, I believe, is new, and I find it very illuminating. There are two studies in this general field now current in Pittsburgh, one is being performed in my laboratory and the other in the laboratory of Dr. Herty. The methods of attack used are somewhat different though they lead to similar results. We have adopted the dilatometer at least for the moment in studying the temperatures of transformation at varying cooling rates and also the rates of precipitation. The first slide shows the type of curve which is obtained on heating and cooling on 0.40 per cent carbon steel, prepared by Howard Scott of the Westinghouse Electric and Manufacturing Co. from hydrogen-purified iron, melted and alloyed with carbon and poured under hydrogen. The next slide shows the dilatometric cooling curves obtained from this sample at various rates of cooling from 1.3 degrees per minute to 50 degrees per minute. You will see that the $A_{3.2}$ point is greatly affected by the different rates, but that the A_1 point is not much affected. This is quite in conformity with Professor Upton's diagram. The next slide shows the same steel in which the temperature to which the material was heated before cooling was increased in four steps. Evidentally the effect of heterogeneity of which Professor Upton speaks and of grain size plays a role here for the temperature is lower the higher the steel had been heated. The next slide shows the steel prepared in similar way with 0.27 per cent carbon. The effect of heating

at various temperatures in the austenite zone is very evident here also. The next slide illustrates the effect of what might be called metallurgical condition. The upper two curves show the position of the transformation temperatures for cooling rates of 2.7 degrees Fahr. per minute and 22 degrees Fahr. per minute. The steel was prepared by Dr. Herty and had been thoroughly killed with aluminum. It contained 0.25 per cent carbon. The lower two curves are similar but for the material before the addition of aluminum, therefore, for a wild steel. It can be seen that the amount of undercooling is less than for the killed steel. The next slide shows dilatometric curves taken on the wild steel from different temperature points within the austenite range. Apparently the wild steel is not so sensitive to the effect of heat treatment within the austenite range as the previous laboratory pure steels. (These curves will shortly be reproduced in a publication, and for this reason are not given here.—Ed. note.)

The technique adopted by Mr. McBride in Dr. Herty's laboratory is somewhat different from this. In this case the rate of precipitation is studied using the same technique used by Bain and Davenport. The next slide is a summary of the results. We have plotted here the decrease of super-cooling as abscissæ and the percentage of ferrite per minute divided by the grain surface per cubic inch as ordinate. The selection of this unit on the ordinate you will see eliminates the effect of grain size. It was observed in these studies that the ferrite precipitates only at the grain boundaries. Steel Z is an aluminum-killed steel with 0.41 per cent carbon. Steel D is a similar steel with 0.44 per cent carbon. Steel Y is a silicon-killed steel with 0.41 per cent carbon. Steel AD is a silicon-killed steel with 0.40 per cent carbon. All of these data show what might be described as the effect of the metallurgical condition of the steel. Apart from this, ordinary analysis chiefly with respect to carbon is of great importance in determining the rate of ferrite precipitation. It is evident to many of you here that the results of these studies should be of interest in the heat treatment of plates, forgings, and steel castings, especially with respect to normalizing and the slower rates of quenching.

Professor Upton has followed Bain and others in drawing analogies between the reaction for the formation of pearlite and ordinary chemical reactions with respect to rates. While it is quite true that formal compliance can be obtained in this way, I think there are some distinct advantages in analyzing rates such as this from a standpoint of the known mechanics of the reaction. The formation of pearlite from austenite proceeds by the formation of nuclei which grow forming essentially spheroids. The spheroidal nature of the pearlite or troosto-pearlite patches is quite evident in many of Bain's photomicrographs. Evidently if we can set up equations which express the rate of reaction in terms of the known process for the formation of pearlite from austenite, our equations will have a specific physical meaning. This has been done by Göler and Sachs.* I thought it might interest you to see this and to have the advantages of the method pointed out. Bain's curves may be analyzed according to this method. In fact Wever's curves which are given in the diagram are much similar to those of Bain's Fig. 1. It will be noted from the derivation

*F. v. Göler and G. Sachs, "Zur Kinetik von Kristallisationsvorgängen," *Zeitschrift für Physiche*, Vol. 77, 1932, p. 281-286.

of the formula from which the curves were drawn that one factor has been left totally unaccounted for, namely, the decrease in active growing surface of the spheroids by reason of spheroids growing together and thus decreasing the growing surface. I have myself attempted to complete the equation and to draw the full curve, but the methods of analysis are very complicated involving some rather uncertain statistical considerations.

These processes consist in formation of nuclei and growth of nuclei. Assume a constant rate of nuclei formation and a constant rate of growth—constant growth velocity. The volume Φ of a cubical grain at time t whose nucleus formed at time T is:

$$\Phi = 8\ w^3\ (t - T)^3 \quad \ldots\ldots(1)$$

Here we assume the grain to form a cube, and the rate of growth of each of the six faces is w.

For the growth of spheroids $8\ w^3$ is replaced by $\frac{4\pi}{3}\ w^3$

Let u (T) be the fraction of the volume unit still not crystallized at any time instant At time T in this volume u (T), dN crystals form, so that

$$dN = c.u(T)\ dT \quad \ldots\ldots(2)$$

These have at time t, according to equation (1) the volumes:

$$\Phi = c.u(T)\ dT\ 8w^3\ (t - T)^3 \quad \ldots\ldots(3)$$

$1 - u\ (t)$ = crystallized volume at time t. This can be obtained by integrating equation (3) for times between zero and t.

This gives the equation

$$u\ (t) = 1 - 8\ cw^3 \int_0^t u\ (T)\ (t - T)^3\ dT \quad \ldots\ldots(4)$$

$$u\ (t) = 1 - \frac{4\pi}{3}\ cw^3 \int_0^t u\ (T)\ (t - T)^3\ dT$$

Substituting values for c and w then gives the curves shown in Fig. 1. You will see that the upper portions of Sachs' curves do not correspond with the experimental curves because the factor of decreasing surface area has been left out of consideration. It appears to me that with a full derivation of the reaction curve in such terms as these the possibility exists, at least, of analyzing the reaction into its component parts, namely, the single factor of rate of nuclei formation and the other single factor of crystallization velocity may be studied. If metals were not opaque, the analysis of reactions of this sort in this way would be much simpler!

Evidently both factors of nuclei formation and crystal growth will be affected by diffusion and Professor Upton properly points out the importance of this. I should think it would be very interesting to attempt some quantitative explanation for the effects of manganese, nickel, and other alloying elements on rates of reaction. It is barely possible that the effect of these elements on rates of diffusion might go a long way to explain the retardation in the reaction which alloying elements exert.

While it is quite legitimate to discuss the pearlite reaction on this basis since it proceeds in such an orthodox fashion as indicated, the martensite reaction is in a class by itself. Here the reaction does not proceed by the formation of nuclei and their subsequent growth but proceeds by a shift in the lat-

tice, a shift in the nature of a shear parallel to the octahedral planes of the austenite. The full mechanics of this shift are now well understood. Both the tetragonal phase and the ferrite possess unique orientations with respect to the mother austenite. Each orientation of austenite is capable of producing 24 new orientations of either the tetragonal phase or the ferrite. It has been generally assumed, especially by German workers, that the martensite reaction dif-

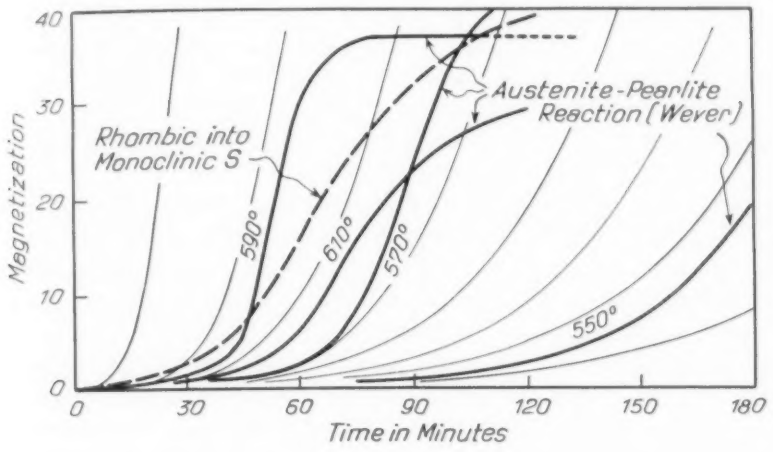


Fig. 1

fers from a pearlite reaction by the fact that the pearlite reaction generates no specific orientations in the pearlite. However, this question has been restudied in our laboratory this year, and it has been found very recently that the ferrite in pearlite possesses an orientation which it inherits directly from the original austenite much as the tetragonal phase and the ferrite in martensite inherit their orientations from the original austenite. There is a difference, however, between the two reactions from a purely crystallographic point of view apart from their characteristic reaction rates, namely, the orientations possessed by ferrite in pearlite with respect to the mother austenite are not those displayed by the tetragonal phase and ferrite in martensite with respect to the austenite. Accordingly we have two different crystallographic mechanisms for the decomposition of austenite. Whether such crystallographic points of view will ultimately be of much use in the analysis of rates, of course still remains to be seen.

Written Discussion: By Gilbert E. Doan, associate professor of physical metallurgy, Lehigh University, Bethlehem, Pa.

It is difficult for me to conceive of a paper better suited to an audience interested in the heat treatment of steel than the one just presented by Professor Upton. The interpretations of Professor Upton are quite worthy of the experimental results, especially the classical ones of Davenport and Bain, on which they are based. In view of the limited time available for discussion, I shall attempt to speak upon several points which are of interest to many of you rather than to discuss matters of greater detail.

In the first place, I agree with Dr. Mehl that the X-ray method should be given credit with showing a difference between the beta and the beta-prime

phases in brass. The presence of a super-lattice in the latter phase seems to me adequate indication of a separate phase.

The method of locating the true Ac and Ar points which Professor Upton has used is, I think, also worthy of attention because of the very great importance of these temperatures. His method of determining the exact eutectoid composition also is a valuable one.

In connection with Fig. 7 and the discussion of these quasi-equilibrium diagrams, I must admit that it is difficult for me to visualize an austenite solid solution precipitating a constituent in which it is not saturated, that is, when it is saturated actually in another constituent—for this is what we are led to believe if this diagram is interpreted according to Professor Upton. This follows from Professor Upton's statement that pearlite does not supercool as much as either proeutectoid alpha iron or Fe_3C.

The author has also made quite clear to us again the effect of holding a steel in the austenite region long enough for the composition to become practically uniform in all parts of each grain. He has pointed out again the difference in composition of austenite held at different temperatures and also the effect of grain size in determining how long it is necessary to hold the steel in the austenite region. These well known requirements of heat treatment are clearly treated by the author in terms of the super-cooling lag of the martensite transformation, shown also at the lower right-hand part of Fig. 7.

I am especially pleased with the author's treatment of the rate of transformation of austenite at various sub-critical temperatures, as one influenced by (a) the absolute temperature and (b) the distance of the reaction temperature from equilibrium temperature. This is a perfectly fundamental viewpoint and its value is revealed in the good correlation obtained in the author's calculations, and his graphs (Figs. 12 and 13).

Concerning the view that the hardness of martensite is due alone to the fineness of grain size, it seems to me that the author is on rather dangerous ground in his conclusion. Sachs' relationship of grain size and hardness shows a large effect of grain size as we approach a single crystal, but very little increased hardening when the grain size becomes finer. It may be that hardness is *accompanied* by a fine size; but in view of the modern knowledge of age hardening, it seems to me doubtful that the hardness of martensite is due to grain size alone.

Author's Closure

Rarely does discussion add so much to a paper as it did in this case. Particular thanks are due to Dr. Mehl.

The author does not know why pearlite should supercool less, or form faster, than its components do alone. Such seems simply to be the fact. Dr. Johnston states that the driving force to form nuclei varies as $\sqrt[3]{T_c - T}$, which would give basis for the "law of supercooling" suggested by the author purely as empirical. Mr. Cowle confirms the finding of 720 degrees Cent. for A_{c_1}. Dr. Schwartz will find that while carbon is too slightly soluble in α or β iron to affect the magnetic change point, other solutes, for example Ni, Mn,

Si, P, do considerably affect it. The author's Fig. 2 does not violate the phase rule.

Between the author and Dr. Mehl discussion might be endless. The specification of a phase as a space lattice pattern seems incomplete; the nature of the atoms occupying the points of the lattice would seem also important. Atoms of α and β iron are not alike. The curve of "orderliness" versus temperature for β and β prime in brasses is exactly like, in form, the curve of permeability (in strong fields) versus temperature in α and β iron, except that the high and low temperature ends are transposed. Magnetic testing has fallen into a habit of taking magnetometer readings "on the fly" while temperature is rising or falling. While this may be justifiable from the way magnetism varies with temperature in an element of material (and that is arguable), it involves, near the magnetic change point, trouble from the fact that different parts of the test piece are at different temperatures, and the magnetometer gives an integrated reading of all the parts. Hence the procedure causes a rounding of what might, perhaps would, be sharp corners on the permeability-temperature curves. Magnetism often shows temperature hysteresis; look at the so-called irreversible nickel and manganese steels, or the magnetic change of Fe_3C.

The nickel alloys of iron may illustrate another possibility also. We cannot make artificially the structures of meteorites—it takes too long. The equilibria of the Fe-Si alloys are likewise slow at even medium Si; hence they may act as if the line F B (Fig. 2) extended downward to the right, unless they are given a very long anneal at the temperature of test. This would explain the low temperature X-ray findings.

The Göler and Sachs equations for reactions in the solid are of a form that can characterize only the beginning of a reaction in the solid. But they are on the right track. Two time rates are involved, that of formation of nuclei and that of growth upon the nuclei. Gaseous reactions would lack, perhaps, one of these. In the case of pearlite formation, the nucleus formation rate is slow compared to the growth rate; in the case of martensite formation, the nucleus formation rate is high compared even to the high growth rate. Further, in the case of martensite, growth is much more rapid in two dimensions than in the third. The fact that the form of the curve of pearlite formation versus time is independent of the temperature shows that temperature affects alike, by both the functions of T abs. and (T_c-T), the nucleus formation rate and the growth rate—a most important point for the final mathematical statement of our problem.

AN ANALOGY BETWEEN PLASTIC DEFORMATION AND CERTAIN COOLING RATES IN CAUSING "PREMATURE" PRECIPITATION IN SUPERSATURATED SOLID SOLUTIONS—THE INCUBATION PERIOD—PART I

By J. L. Burns

Abstract

This paper reports a study made on the age-hardening of duralumin. The effect of cooling rate upon age-hardening and upon the incubation period was investigated. It was found that if a supersaturated solid solution is plastically deformed immediately after the quenching operation then aging begins earlier, there is no incubation period and the final hardening due to precipitation is less. It was also found that if a particular rate of cooling was used in quenching from the temperature of maximum solubility then the same results were obtained. From this it is concluded that plastic deformation does not increase the rate of hardening but merely causes hardening to start earlier.

Introduction

SINCE the work reported in this paper was begun, two very interesting papers have appeared on the effect of plastic deformation upon quenched duralumin. Fraenkel[1] and, a little later, Meissner[2] published data on this subject. Briefly, they concluded that cold work hastens the age-hardening of duralumin.

In the present paper a study was made of this phenomenon and it has been concluded that this statement requires modification. It was also found that the results obtained by plastic deformation may be duplicated by particular cooling rates.

Method of Deformation

In a recent paper by Professor Sauveur and the writer[3] a simple and convenient method for the study of strain-hardening suscepti-

[1]W. Fraenkel, "Beeinflussung de Vergütung durch Recken nach dem Abschrecken," *Zeitschrift fur Metallkunde,* Vol. 24, 1931, p. 172-76.

[2]K. L. Meissner, "Einfluss der Kaltverdichtung auf die Aushärtung von Duralumin," *Zeitschrift fur Metallkunde,* Vol. 24, 1932, p. 88-9.

[3]Albert Sauveur and John L. Burns, "A Method for Studying Strain Hardening Susceptibility and Aging After Cold Work Deformation," *Metals and Alloys,* January 1933, p. 6.

The author, who is a member of this Society, is metallurgist with the Republic Steel Corporation at Chicago. Manuscript received March 31, 1934.

bility and aging after plastic deformation was outlined. The method, as applied to a study of age-hardening after plastic deformation, is to make two Brinell impressions under a given load. A Rockwell "B" hardness reading is immediately made at the bottom of one of the impressions. The other impression is subjected to the aging treatment, and then the Rockwell B hardness is observed at the bottom of this impression. In effect a hardness reading of the material as "cold-worked," and "as-aged" after the cold working is obtained.

Effect of Plastic Deformation Upon the Ultimate Hardening of Duralumin

Dr. Merica[4] points out, that age-hardening after quenching may result either from a migration of solute atoms to positions within the lattice of the supersaturated solution, probably favorable to precipitation, or it may result from true precipitation. Since either phenomenon is one of diffusion, age-hardening is the result of a diffusion process. The rate of hardening and the diffusion rate will be used interchangeably in this paper, as in reality one is the result of the other.

In order to study the effect of plastic deformation upon diffusion, two samples of duralumin, having the following composition, were quenched from 510 degrees Cent. (950 degrees Fahr.) in water.

Copper	4.0 Per Cent	Silicon	0.50 Per Cent
Magnesium	0.50 Per Cent	Aluminum	Remainder
Iron	0.50 Per Cent	Sizes of Samples,	½x½x5 Inches

One was allowed to age for 48 hours at room temperature and the other was plastically deformed immediately after quenching and allowed to age during the same 48 hours at room temperature.

After the aging was completed, the first sample was deformed under the same load which was used in deforming the second test specimen. The hardness was read immediately. The hardness of the second bar, which had been cold-worked immediately after quenching, was also read after the 48 hours aging. In effect, the first bar was aged in the normal fashion after quenching. The cold working at the finish was merely to make the hardness results comparable to those of the second bar which had been aging in a plastically deformed state. Or, again, the relief or supersaturation

[4] Paul D. Merica, "Age Hardening of Metals," *Transactions*, Institute of Mining and Metallurgical Engineers, Vol. 99, 1932, p. 13.

in normal metal is compared to the relief or supersaturation in plastically deformed metal.

The results are shown in Table I and plotted in Fig. 1. It seems from these results that diffusion proceeds more easily when the metal is not plastically deformed. Plastic deformation appar-

Table I
Effect of Plastic Deformation Upon Diffusion of Duralumin

Treatment A:			Treatment B:		
1. Quenched from 510 degrees Cent. in water			1. Quenched from 510 degrees Cent. in water		
2. Aged 48 hours at room temperature			2. Worked under specified load in Brinell machine		
3. Worked under specified load in Brinell machine			3. Aged 48 hours at room temperature		
4. Rockwell B in Impression immediately.			4. Rockwell B in Impression		
Load in Kilograms	Final Hardness, Rockwell B	Width of Impression in Millimeters	Load in Kilograms	Final Hardness, Rockwell B	Width of Impression in Millimeters
125	85.8	1.45	125	80.3	1.90
200	88.4	1.80	200	81.7	2.20
500	90.8	2.50	500	82.5	2.90
1000	91.3	3.30	1000	82.5	3.90

ently slows the diffusion process, and, therefore, the age-hardening process[5, 5a].

It should be indicated that the metal which had been aged normally (without plastic deformation) had increased in hardness, so that when it was finally deformed under the same load as the freshly quenched metal, the degree of deformation was less. This fact only exaggerates the conclusion already drawn. This objection may be overcome, however, by running a series of deformations and using the depth or the width of the impression as a measure of plastic deformation. Then the final hardness in each case may be plotted against the width of the impression. This is done in Fig. 1.

Diffusion Rate Versus the Degree of Plastic Deformation

A study of the effect of the degree of plastic deformation upon

[5]G Sachs, "Suppressed Constitutional Changes in Alloys," *Transactions*, Institute of Metals Division, American Institute of Mining and Metallurgical Engineers, 1931, p. 39.

Dr. Sachs shows a figure from Schmid and Wasserman indicating the hastening of precipitation by a deformation of one per cent. As will be shown later, however, this is true only of the early stages of decomposition.

[5a]Both Fraenkel and Meissner have made very interesting studies of the behavior of the tensile properties during the age-hardening of quenched duralumin after plastic deformation. The facts brought out in these reports are in agreement with the findings of the parts of these experiments which they concern. Their conclusion that age-hardening increases the diffusion rate is disputed in these experiments for the reasons to be offered. See footnote 1 and 2.

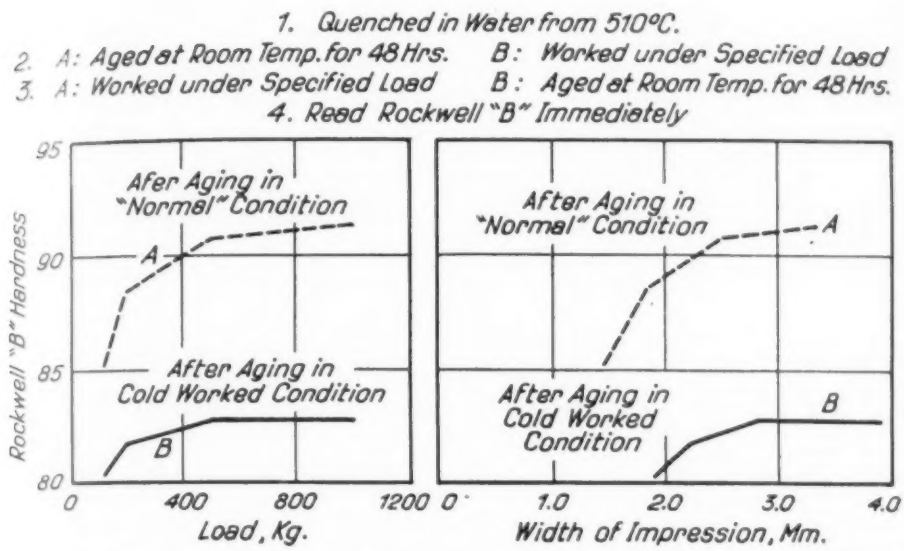


Fig. 1—Rockwell Hardness Values Plotted Against Deforming Load and Width of Impression.

the diffusion rate is also afforded in Fig. 1. The results are plotted in two ways. First, the final hardness is plotted against the deforming load in each case (disregarding the fact that the degree of plastic deformation is less on a harder metal under a given load). This means that the energy used in deforming the metal is the same. Secondly, the final hardness is plotted against the width of the impression. This disregards the energy used in the deformation and assumes that the same deformation is obtained only when the same width of impression results. In other words, the load necessary to obtain comparable impression is disregarded.

The conclusion is the same no matter which values of deformation are used as the abscissae. Increasing deformation decreases the ultimate hardening due to precipitation. The difference is merely in degree, depending upon the abscissae. It is concluded, however, that plastic deformation slows the ultimate diffusion, during the breakdown of supersaturated solutions.

Further Study of the Effect of Plastic Deformation Upon the Diffusion Rate—The Incubation Period

One sample was plastically deformed immediately after quenching and another was aged, and then deformed. This procedure is the same as in the preceding tests.

Instead of allowing the complete aging to take place before

comparison was made, several readings were made between zero and the final readings in order to obtain an idea of the effect of cold work upon the early stages of aging—and upon the incubation period. Table II and Figs. 2 and 3 illustrate this effect.

It can be seen that diffusion is apparently hastened by cold work during the early stages of aging. This can be traced to a

Table II
Effect of Plastic Deformation Upon Diffusion of Duralumin

Treatment A
1. Quenched in water from 510 degrees Cent. (950 degrees Fahr.)
2. Cold-worked under specified load in Brinell
3. Aged for specified times at room temperature
4. Rockwell B read immediately at bottom of the Brinell Impression

125 Kilograms	500 Kilograms	1000 Kilograms	Aging Time at Room Temperature After Quench
61.8	72.5	73.5	Zero
70.3	78.5	78.3	2 Hours
74.0	80.0	80.5	5½ Hours
77.0	80.0	80.8	24 Hours
77.8	80.5	81.5	48 Hours

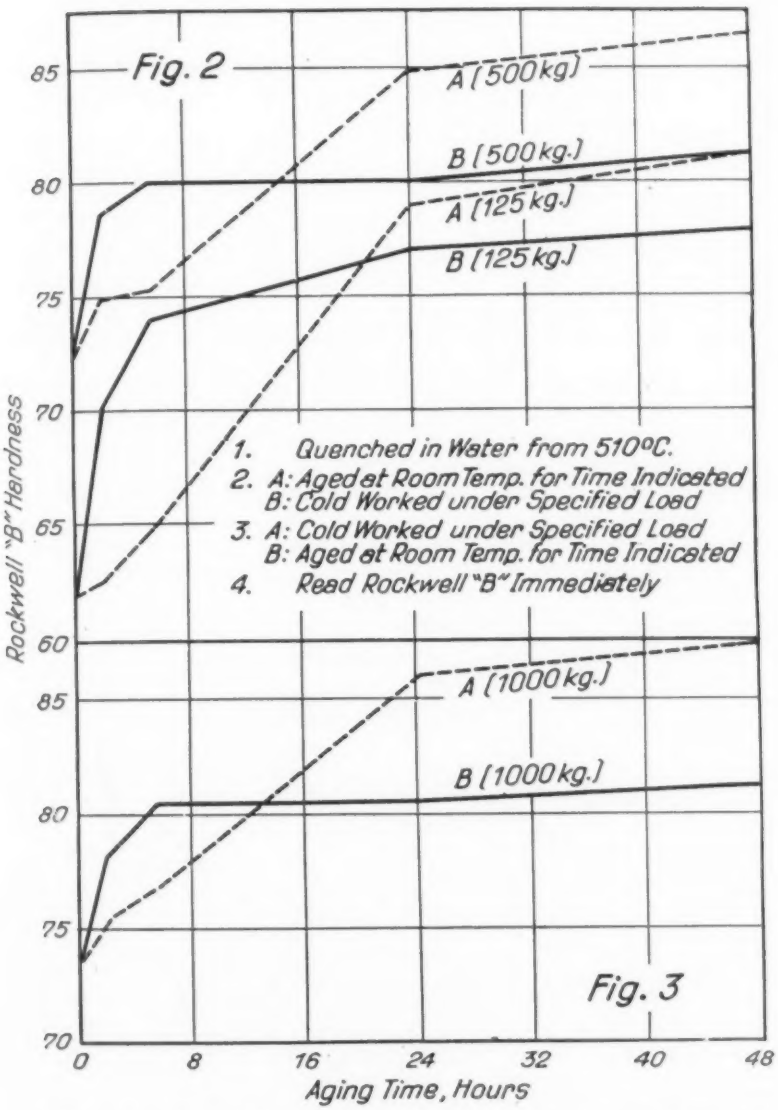
Treatment B
1. Quenched in water from 510 degrees Cent. (950 degrees Fahr.)
2. Aged for specified time at room temperature
3. Cold-worked in Brinell machine under specified load
4. Rockwell B read immediately at bottom of the Brinell Impression

125 Kilograms	500 Kilograms	1000 Kilograms	Aging Time at Room Temperature After Quench
61.8	72.5	73.5	Zero
62.5	74.9	75.5	2 Hours
64.8	75.2	76.9	5½ Hours
79.0	84.8	86.0	24 Hours
81.1	86.6	87.0	48 Hours

shortening of the incubation period by the plastic deformation. Diffusion in the cold-worked metal then slows down, and the aging in the quenched metal (not cold-worked metal) surpasses it, as illustrated.

Effect of Cooling Rate Upon Age-Hardening and Upon the Incubation Period

The diffusion of solutions varying in degree of supersaturation was studied without the effect of plastic deformation. The results are tabulated in Table III and plotted in Fig. 4. Samples of duralumin were quenched in water, oil and air, from 510 degrees Cent. (950 degrees Fahr.). It is interesting, first, to study the hardness obtained immediately after each treatment. The air-cooled sample has the greatest hardness and the oil-cooled sample has the second greatest hardness. The water-quenched sample is softer than either.



Figs. 2 and 3—Effect of Plastic Deformation Upon Diffusion of Duralumin. See Table II.

The only conclusion as to the reason for these values is that precipitation or knot-formation has taken place in the quenching bath in the case of the air- and oil-quenched samples. The rate of cooling was sufficiently slow to throw some of the solute out of solution, but not slow enough to allow much agglomeration. In the case of the water-quench, probably very little material, if any, was thrown out of solution, because of the drastic cooling. In furnace cooling the rate was slow enough to throw the solute out of solution and to allow agglomeration to proceed at the same time.

Table III

Effect of Cooling Rate Upon Age-Hardening and Upon Incubation Period

Rockwell B After Specified Aging Time at Room Temperature

Cooled in	Immediately After Cooling	6½ Hours	25 Hours	30 Hours	31 Hours
Water	34.8	42.1	65.3	66.7	69.3
Oil	41.0	58.4	65.1	66.4	68.2
Air	51.1	51.9	55.2	56.9	60.5
Furnace	30.5	31.6	31.1	31.7	35.2

During the subsequent aging at room temperature, the behavior of the oil-quenched sample is very striking in one instance. Between the zero and the 6½-hour reading the increase in hardness is greater in the case of the oil-quenched sample than in the water-quenched sample. Other than this reading, the rate of hardening

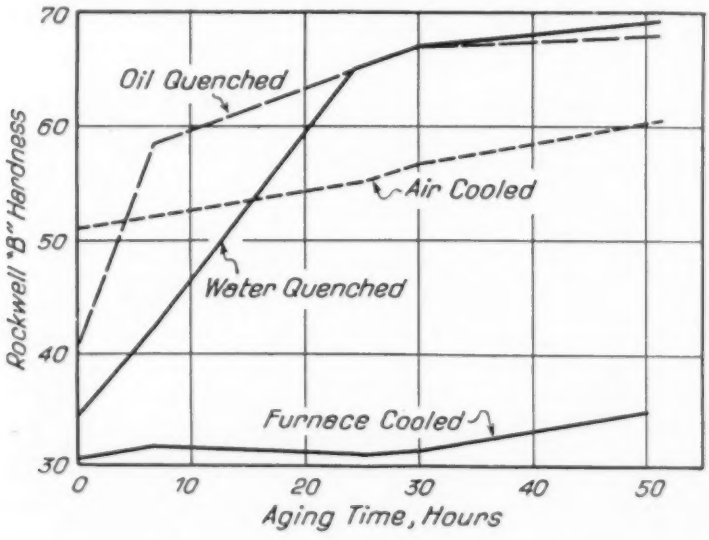


Fig. 4—Effect of Cooling Rate Upon Age-Hardening and Upon Incubation Period. See Table III.

increases, with the degree of supersaturation, preceding the hardening. The explanation of the one apparently anomalous reading is probably connected with the so-called incubation period. The incubation period is a period of rest immediately after quenching during which no hardening ensues[6]. The oil quench apparently shortens or practically obliterates this incubation period. This striking occur-

[6]Zay Jeffries, Discussion of Reference 5, p. 50.

Dr. Zay Jeffries, in his discussion of the paper by Sachs, indicates that the incubation period is not really one of zero activity. In his investigations and in those of others, which he mentions, a slight softening occurs during this period. He believes that this is due to the "transition" which is occurring. The "transition" causes the forces of diffusion and compound formation to assist the slip movement during deformation.

rence causes one to wonder why the incubation period is longer in the case of the more highly supersaturated solution. One would assume that the urge for the decomposition of the supersaturated solution would be greater in the water-quenched sample. The obvious answer is that precipitation has already begun in the oil quenching bath[7] and that now the diffusion of the solute may proceed without hesitation. It is closely analogous to the supersaturated salt solution where the addition of a crystal will allow crystallization to proceed. But crystallization must first be started. It is quite conceivable that the incubation period is merely a period during which diffusion is awaiting the proper conditions to proceed. If these conditions are provided in the quenching bath (as in oil), then no such incubation period is necessary. Might one infer then, that whenever an incubation period exists no precipitation has taken place in the quenching bath?[8]

Conclusions

(1) If a supersaturated solid solution is plastically deformed immediately after the quenching operation:

1. Aging begins earlier
2. There is no incubation period
3. The final hardening (due to precipitation) is less.

(2) If a particular rate of cooling is used in quenching from the temperature of maximum solubility:

1. Aging begins earlier
2. There is no incubation period
3. The final hardening will usually be less.

(3) From (1) and (2) it is concluded that plastic deformation does not increase the rate of hardening (it actually decreases the hardening rate) but merely causes hardening to start earlier.

(4) Precipitation may take place during a cold working operation or during quenching.

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[7] Albert Sauveur, *Metals and Alloys*, January 1933.

If this reasoning be correct, Professor Albert Sauveur's theory of the hardening of steel by quenching from the gamma range receives strong support from the findings of these experiments. He believes that the iron carbide precipitates during the quenching operation due to the great decrease in solubility of carbon in going from gamma to alpha iron.

[8] C. S. Smith, Discussion of Reference 5, p. 48.

This is an important point, for, as Dr. C. S. Smith, in his discussion of Dr. G. Sachs' paper, pointed out that X-ray measurements are often erroneous in defining solubility limits above room temperature. This error is due to our not knowing whether the supersaturated solution has partially decomposed during the cooling operation. A way out of this difficulty may be found in a study of this incubation period.

(5) When an incubation period ensues after quenching, it is suggested that the solute has been retained in its entirety during the quenching operation.

(6) The hardness of quenched steel is probably due to the same cause as that of oil- or air-cooled duralumin, namely, aging during the cooling operation. This analogy, if true, obviates any sharp line of demarcation between ferrous and nonferrous alloys.

Acknowledgment

This investigation was carried out under the guidance of Dr. Albert Sauveur, Gordon Mackay professor of Metallurgy at Harvard University. The author wishes to express his deepest appreciation to Professor Sauveur for his constant interest and encouragement. He has drawn freely from Professor Sauveur's many suggestions.

QUENCHING STEEL IN HOT LEAD

By T. P. Hughes and R. L. Dowdell

Abstract

This paper compares the mechanical properties of two plain carbon steels of 0.34 and 0.49 per cent carbon quenched in molten lead with those obtained by quenching and tempering. Results indicate that standard tensile test bars quenched in lead at 650 degrees Fahr. (345 degrees Cent.) have approximately the same mechanical properties and microstructure as those quenched in oil followed by tempering at 1200 degrees Fahr. (650 degrees Cent.). Figures are given showing the effect of variations in the mechanical properties by changes in the initial quenching temperature and also in the temperature of the lead quenching bath.

Introduction

THE purpose of this investigation was to study the relative merits of two heat treating methods; namely, 1. quenching in a suitable medium followed by tempering, and 2. quenching in lead maintained at various temperatures, thus hardening and tempering simultaneously. The practice of hardening and tempering steel as now almost universally carried out in industry is to quench the properly heated steel in a suitable coolant until it reaches a certain temperature, then remove it, and reheat it to a predetermined temperature in order to temper it.

Some late contributions to the theory of hardening call attention to the possibility of obtaining the structures (troostite or sorbite) resulting from tempering by cooling the steel at a modified or slower rate than that obtained by quenching it in oil or water. This, it is asserted, might be effected by the use of a coolant maintained at a desirable temperature. In the few studies of this phenomenon reported, use has been made of materials such as lithium nitrate (1)*, oils (2), hot water (3), acids (4), alkalis (5), aqueous solutions (6) (7), lead (8) and salts (9).

Modifying the critical cooling rate of carbon steel from the

*The figures appearing in parentheses refer to the bibliography appended to this paper.

Of the authors, T. P. Hughes is instructor in mechanical engineering, and R. L. Dowdell is professor of metallography, University of Minnesota, Minneapolis, Minn. Manuscript received March 12, 1934.

temperature of stable austenite results in the production at ordinary temperatures of microstructures which vary in hardness directly as the rate of cooling. Increasing the cooling rate suppresses consecutively the temperature of the transformation of the austenite to form these various structures.

The theory that rapid cooling lowers the critical points was proposed by LeChatelier (10) in 1897; then again in 1911 it received attention by Grenet (11). Later in 1917, it was generally realized that the effect produced by rapid cooling was caused by the lowering of these critical points. In that year a summary of his work on alloy steels, showing the connection between the initial temperature, the rate of cooling, and the temperature of the critical points in these steels, was published by Portevin (12). Later, a paper by Portevin and Garvin (13) showed that in carbon steels the transformation took place at a low temperature during quenching. This was later confirmed by the work of Chevenard (14), Dejean (15) and Honda and his co-workers (16).

Dejean found two such critical temperatures in martensitic steels of both the plain carbon and alloy grades. The first of these appears at 1218 degrees Fahr. (660 degrees Cent.) (Ar′) and the second between 392 and 752 degrees Fahr. (200-400 degrees Cent.) (Ar″). The latter he found only when the steel contained martensite. These two points were also found by Chevenard (17) and later by Matsushita (18) who measured the changes in length which took place during cooling. They also found that the position of the Ar″ was affected not only by the rate of cooling but by the carbon content as well. In low carbon steels, Matsushita stated that it appears at about 932 degrees Fahr. (500 degrees Cent.) while in the high carbon steels it appears at a much lower temperature or between 392 and 752 degrees Fahr. (200-400 degrees Cent.). Hanemann and Schrader (19) stated that in high carbon steels, the expansion comes below 392 degrees Fahr. When the Ar′ and the Ar″ points are both present, the constituents troostite and martensite will be found in the microstructure. With an accelerated cooling rate the Ar′ disappears and only the Ar″ remains. This will result in the structure being wholly martensitic.

In view of the large volume of steels receiving the hardening treatment and the accepted fact that the stresses induced by quenching for hardness often lower the physical properties due to internal cracks, it is significantly astonishing that a greater amount of research

should not have been directed in an effort to obtain desirable structures and properties by a single treatment. A modified cooling, because of its less drastic character, would tend to greatly reduce these internal stresses since it would permit the changes in volume to take place while the steel still possessed some degree of plasticity.

The industrial practice called "patenting" in which a high carbon wire is quenched in molten lead from a high temperature is a modified form of a retarded quench. The cooling of wire in this process in which only small diameters are employed is not, however, wholly analogous to the hardening and tempering of large and intricate sections of steel of low or high carbon content as encountered in industry.

A carbon steel 0.192-inch diameter wire of 0.80 per cent carbon was quenched by Lewis (9) from 1500 degrees Fahr. (815 degrees Cent.) in fused salt at 450 degrees Fahr. (230 degrees Cent.), and upon withdrawal the steel was nonmagnetic and soft but became strongly magnetic and extremely hard and brittle on cooling in air. The Rockwell "C" hardness also increased from 24 to 26 in the "as quenched" condition to 58 to 60 in the cold condition. Apparently the steel was austenitic after quenching at this temperature but changed to martensite during air cooling. Increasing the temperature of the salt bath from 450 to 650 degrees Fahr. (230-345 degrees Cent.) caused a change in the reaction. After one-half minute and also 5 minutes immersion in the bath at this temperature, the contraction of the specimens was found to be continuous and gave no evidence of the formation of martensite. The microstructure was said to be entirely sorbitic. Evidently the rate of heat abstraction by the bath at this temperature was not sufficiently rapid to cause the Ar″ phenomenon though the final temperature of the bath was below that required for the formation of martensite.

In a study of the microstructure of rapidly and slowly cooled steels, Robertson (20) was able to obtain uniform and sequential structures by uniformly varying the rates of cooling. He discovered, however, that so far as crystallographic form is concerned, no relation exists between cooling at different rates and tempering at different temperatures. Further, he concluded that the structures formed by cooling at different rates cannot be obtained by tempering other structures.

Honda (21) working with an 0.89 per cent carbon steel in the form of a short square rod 0.6 x 0.6 x 0.75 inches quenched from

1472 degrees Fahr. in a salt bath maintained at temperatures of 716, 824 and 1040 degrees Fahr. found that the hardness was maximum at a quenching temperature of 230 degrees Fahr. by virtue of the complete martensitization of the steels. The sorbitic structure obtained by this method was as strong as that obtained by the ordinary method of quenching and tempering. He concluded that the new method affords a means of obtaining the tempered structures by a single process without any risk of internal failure in the steels.

Davenport and Bain (22) clearly showed that austenite transformed at subcritical temperatures and their work is thus in agreement with that of Lewis (23). Recently Diergarten (24), and still more recently Daasch (25), investigated the subject of "hot quenching" and reported favorably on its application to the quenching of materials where excessive stresses are to be avoided.

Materials Used in this Study

This study was conducted on two carbon steels of different compositions and of a type used for drop-forged and forged parts, such as wrenches, hooks, steering knuckles, crankshafts, front axles, locomotive connecting rods, main rods and other forgings which are subsequently heat treated.

	Chemical Composition Per Cent				
Steel	Carbon	Manganese	Silicon	Phosphorus	Sulphur
A	0.34	0.44	0.04	0.016	0.04
B	0.49	0.78	....	0.018	0.045

Analyses by Mines Experiment Station, University of Minnesota.

Preparatory Work

The heat treating temperatures used in this study are based on considerable preparatory work undertaken to check the critical points as obtained by thermal analysis and to determine the temperature for quenching in oil, water, and lead in order to produce a steel having the proper hardness. The dimensions of the samples used in these experiments were ¾ x ¾ x ½ inch. These were cut from bars which had been forged to ⅞ inch square with a 200-pound steam hammer from cylindrical stock 2 inches in diameter. After normalizing they were machined on four surfaces to ¾-inch diameter and cut to ½-inch lengths. To facilitate their transfer from the furnace to the quenching medium and to provide convenient means of keeping them under the surface of the lead bath, a hole was drilled

near one corner parallel with the diameter to a depth of about ¼ inch. These were tapped and a rod $\frac{3}{16}$-inch by 6 inches screwed in. After heat treatment, the specimens were cut into halves across their diameters and the surfaces ground. The tests for hardness were made on these ground surfaces.

Test Bars

Preparation—Two methods were used in making the test bars. All bars, excepting those described below, were forged from cylindrical stock, normalized and machined. The ratio of reduction for the tensile bars was approximately 4 to 1 and for the Charpy impact bars about 6 to 1. Forging was done with a 200-pound steam hammer at a dull yellow temperature. In order that any possible surface imperfections might be removed, the size of the forgings provided that at least ⅛ inch of metal could be machined from the bars at the largest diameter. The tensile bars made from the 0.34 per cent carbon steel were machined, ⅛-inch oversize, from stock obtained by sawing a 2-inch diameter bar axially into quarters. This method of preparing bar stock for test pieces has much in its favor since it provides for the elimination of possible variation in composition between the core and the peripheral material.

Grinding Allowance—A grinding allowance of 0.015 to 0.020-inch was made on the reference section of the tensile bars (standard 0.505-inch diameter with threaded ends). This was removed with a fine-grade wheel on a wet grinder cooled by a soluble oil mixed with water. The corner of the grinding wheel had previously been dressed by hand to conform to the radius required on the specimen.

The impact bars were reduced to size on a standard milling machine from forged stock $\frac{9}{16}$ x $\frac{9}{16}$ inch. The holes were drilled with a No. 47 drill in a specially prepared drill jig which facilitated the location of the holes in the middle of the length of the bar and the correct distance from either side. The notches were cut after the bars had been heat treated. The holes were plugged tightly with asbestos before quenching so that no cooling effect was produced through the reduced section. An allowance of 0.010 inch was made for final grinding.

Heat Treatment—All test pieces were heated in a gas-fired muffle furnace 12 x 5 x 17 inches. The quenching in oil and water was accomplished in the usual manner with special care being taken

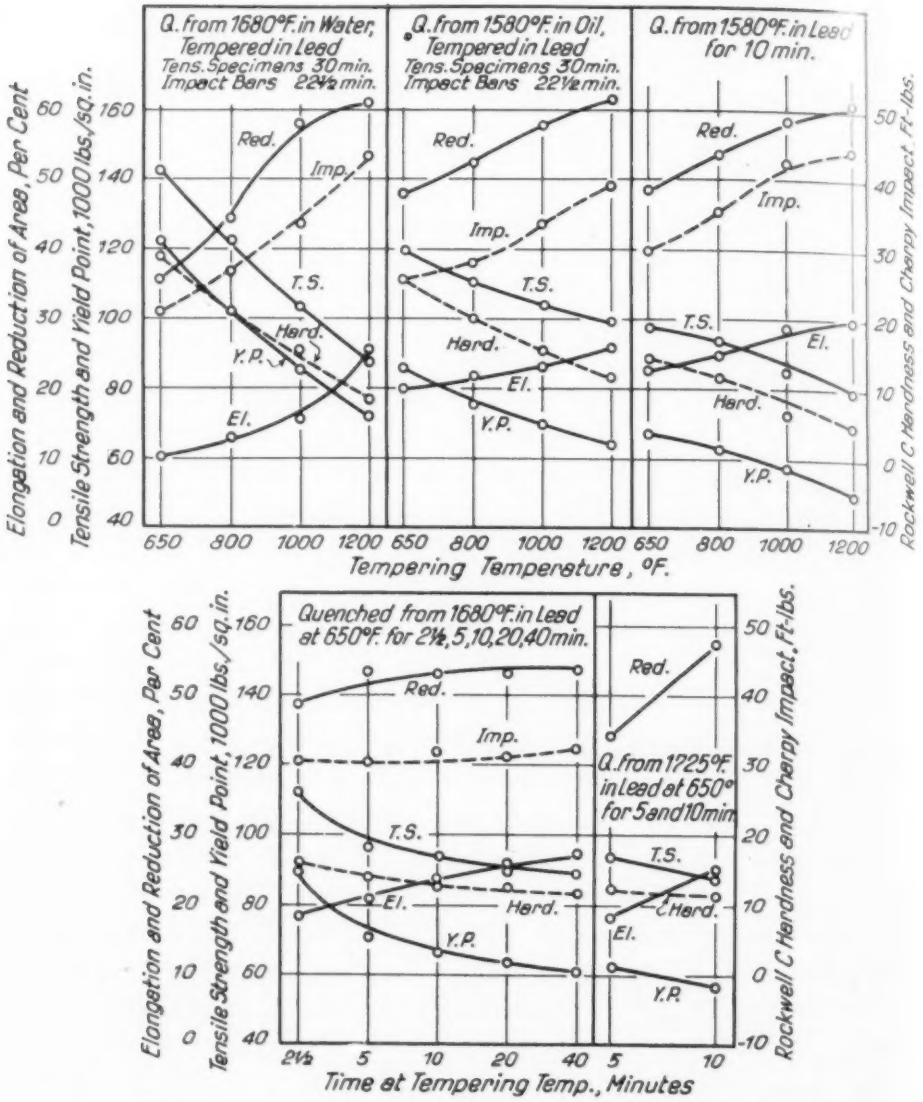

Q. from 1680°F. in Water, Tempered in Lead
Tens. Specimens 30 min.
Impact Bars 22½ min.
Q. from 1580°F. in Oil, Tempered in Lead
Tens. Specimens 30 min.
Impact Bars 22½ min.
Q. from 1580°F. in Lead for 10 min.
Red.
Imp.
T.S.
Hard.
Y.P.
El.
Elongation and Reduction of Area, Per Cent
Tensile Strength and Yield Point, 1000 lbs./sq. in.
Rockwell C Hardness and Charpy Impact, Ft.-lbs.
Tempering Temperature, °F.
Quenched from 1680°F. in Lead at 650°F. for 2½, 5, 10, 20, 40 min.
Q. from 1725°F. in Lead at 650° for 5 and 10 min
C Hard.
Time at Tempering Temp., Minutes

Fig. 1—Mechanical Properties of a 0.34 Per Cent Carbon Steel.

to avoid contact of the specimens with tongs or holders and all samples were cooled to the temperature of the bath. Since the quenching tanks and the lead bath were close to the furnace, the transfer of specimens was accomplished in approximately two seconds which did not allow any appreciable drop in temperature. The samples were vertically quenched in the coolants and in the direction of their greatest length. The only movement in the baths of oil and water was a slow up and down movement and no attempt was made to stir vigorously to accelerate cooling. Owing to the comparatively sluggish condition of the lead, movement of the

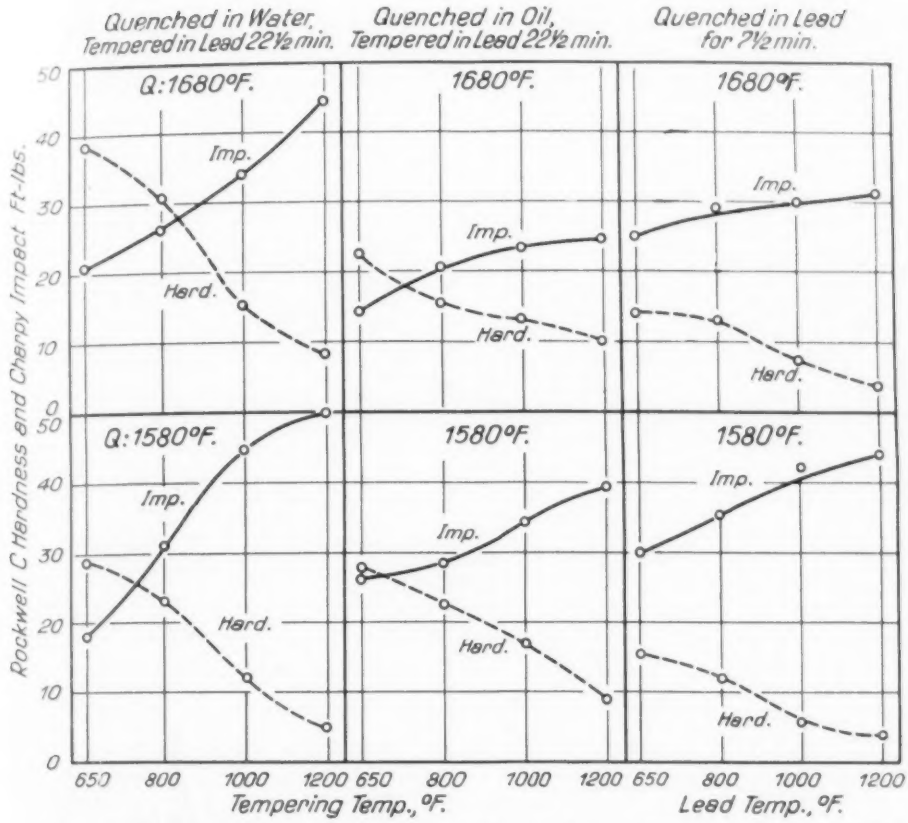


Fig. 2—Heat Treatment, Hardness and Charpy Impact Properties of a 0.34 Per Cent Carbon Steel.

samples in this medium was difficult and therefore was not done. The water used was Minneapolis city tap water. Its temperature was maintained at 70 degrees Fahr. by renewal. The oil was a standard medium light soluble quenching oil and its temperature was maintained at 70 degrees Fahr. by means of a cold water coil inserted in the tank. The volume of the oil and water coolants was approximately 30 and 10 gallons respectively.

In order to keep the specimens immersed in the molten lead, a special tong was made to grip the tensile bars only at the ends and this was immersed in the lead with the bar. The impact bars were wired together so that two specimens might be cooled simultaneously and yet be kept 2 inches apart. A pointed tong was fastened to the wire between the bars and immersed in the lead with them.

All temperatures were determined with a portable potentiometer using a chromel-alumel thermocouple. The lead container of cast steel was gas heated and contained about 75 pounds of lead.

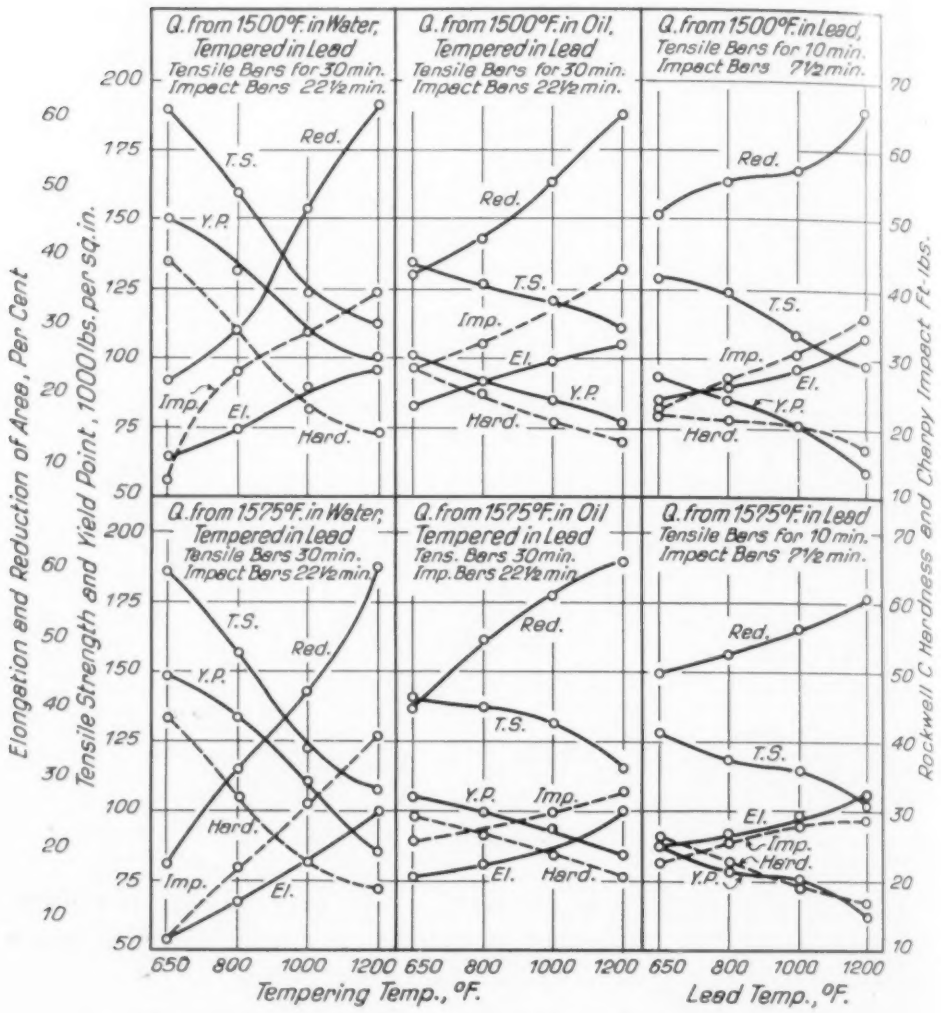

Q. from 1500°F. in Water, Tempered in Lead
Tensile Bars for 30 min.
Impact Bars 22½ min.
Q. from 1500°F. in Oil, Tempered in Lead
Tensile Bars for 30 min.
Impact Bars 22½ min.
Q. from 1500°F. in Lead,
Tensile Bars for 10 min.
Impact Bars 7½ min.
Q. from 1575°F. in Water, Tempered in Lead
Tensile Bars 30 min.
Impact Bars 22½ min.
Q. from 1575°F. in Oil Tempered in Lead
Tens. Bars 30 min.
Imp. Bars 22½ min.
Q. from 1575°F. in Lead
Tensile Bars for 10 min.
Impact Bars 7½ min.
Red.
T.S.
Y.P.
El.
Imp.
Hard.
Elongation and Reduction of Area, Per Cent
Tensile Strength and Yield Point, 1000 lbs. per sq. in.
Rockwell C Hardness and Charpy Impact Ft.-lbs.
650 800 1000 1200
Tempering Temp., °F.
Lead Temp., °F.

Fig. 3—Mechanical Properties of a 0.49 Per Cent Carbon Steel.

The practice followed in the heating of all test bars was to place them in the furnace after it had attained a temperature of 1100 degrees Fahr. (595 degrees Cent.). They then were allowed to absorb the furnace temperature while the door was partly open before further heat was applied. The rate of heating was controlled so that sufficient time was allowed to insure good uniformity up to the quenching temperature. In addition, a "soaking" period was allowed. After each "heat" the furnace was allowed to cool to 1100 degrees Fahr. (595 degrees Cent.) before subsequent samples were inserted. In order that the specimens might be quenched from the predetermined temperature and to avoid too long exposure at temperature, only two tensile bars and only

Table I

Heat Treatment, Hardness and Tensile Properties of a 0.34 Per Cent Carbon Steel*

Tensile bars 0.505-inch diameter gage.

Quench Temp. Deg. Fahr.	Heat. Time (Mins.)	Quench Medium	Temp. of Medium Deg. Fahr.	Tempering Temp. Deg. Fahr.	Temper. Time (Mins.)	Tensile Strength Lbs./Sq. In.	Yield Point	Elong. Per Cent in 2 Inches	R. A. Per Cent	Rock. C Hardness
1580	40	Water	70.0	....	....	137,125	.....	4.5	4.6	46.0
1580	40	Oil	71.5	....	....	110,250	75,760	21.8	55.7	20.0
1580	40	Oil	71.5	650	30	120,000	85,300	18.5	47.5	24.8
1580	40	Oil	71.5	800	30	110,187	76,625	21.0	53.3	18.0
1580	40	Oil	71.5	1000	30	102,687	70,875	23.4	58.5	14.5
1580	40	Oil	71.5	1200	30	100,150	65,200	25.1	60.1	14.4
1580	40	Lead	650	....	10	98,300	68,500	23.4	49.9	13.9
1580	40	Lead	800	....	10	95,950	63,350	25.6	54.6	11.8
1580	40	Lead	1000	....	10	86,957	58,500	29.7	59.2	8.6
1580	40	Lead	1200	....	10	80,775	50,875	30.3	61.5	5.7
1680	40	Water	70	650	30	140,250	120,500	9.2	35.0	27.4
1680	40	Water	70	800	30	122,500	108,200	12.5	44.9	35.0
1680	40	Water	70	1000	30	103,750	88,000	15.6	58.0	19.4
1680	40	Water	70	1200	30	86,750	71,000	25.0	63.0	11.6
1725	40	Lead	650	....	5	95,000	62,050	18.7	44.9	12.7
1725	40	Lead	650	....	10	89,000	51,750	25.0	58.0	12.2
1680	40	Lead	650	....	2.5	110,250	90,250	18.7	49.7	17.5
1680	40	Lead	650	....	5.0	95,700	70,250	21.8	53.8	11.7
1680	40	Lead	650	....	10.0	94,625	66,100	23.4	53.8	12.7
1680	40	Lead	650	....	20.0	92,675	63,200	25.0	53.8	12.2
1680	40	Lead	650	....	40.0	89,925	60,000	27.0	53.8	10.4

*These figures represent the averages of two or more bars.

Table II

Heat Treatment, and Tensile Properties of a 0.49 Per Cent Carbon Steel*

Tensile bars 0.505-inch diameter gage.

Qch. Temp. °F.	Heating Time (Mins.)	Quench Medium	Temp. of Quench °F.	Temper Temp. °F.	Temper Time (Mins.)	Temper Med.	Rock. "C" Hdness.	Tensile Strength (Lbs./Sq. In.)	Yield Point	Elong. % in 2 In.	Red. of Area %
1500	40	Water	70	650	30	Lead	44.0	191,000	150,000	10.9	21.0
1500	40	Water	70	800	30	Lead	35.0	161,400	136,250	14.0	28.8
1500	40	Water	70	1000	30	Lead	22.5	123,375	111,000	20.3	47.1
1500	40	Water	70	1200	30	Lead	19.5	113,250	102,750	23.4	61.3
1500	40	Oil	70	650	30	Lead	29.1	135,900	100,250	18.7	38.0
1500	40	Oil	70	800	30	Lead	25.5	127,000	93,100	22.1	42.5
1500	40	Oil	70	1000	30	Lead	21.7	121,000	85,000	24.8	50.2
1500	40	Oil	70	1200	30	Lead	18.2	110,550	76,000	27.0	60.5
1500	40	Lead	650	....	10	....	22.0	128,000	93,750	18.7	45.7
1500	40	Lead	800	....	10	....	21.0	124,300	82,250	20.3	50.6
1500	40	Lead	1100	....	10	....	20.7	117,075	75,875	23.1	52.2
1500	40	Lead	1200	....	10	....	17.2	98,975	59,750	28.1	60.1
1575	40	Water	70	650	30	Lead	43.7	190,000	149,000	6.2	17.7
1575	40	Water	70	800	30	Lead	32.0	157,850	133,500	12.5	31.8
1575	40	Water	70	1000	30	Lead	22.6	123,325	109,350	18.0	42.5
1575	40	Water	70	1200	30	Lead	19.5	108,050	91,500	25.0	60.8
1575	..	Oil	70	650	30	Lead	29.0	138,475	105,000	15.6	40.4
1575	..	Oil	70	800	30	Lead	27.0	137,950	100,000	17.1	53.8
1575	..	Oil	70	1000	30	Lead	25.2	133,125	92,000	18.7	56.8
1575	..	Oil	70	1200	30	Lead	21.0	113,000	85,000	25.0	61.8
1575	40	Lead	650	....	10	....	26.7	129,350	87,500	20.2	45.5
1575	40	Lead	800	....	10	....	22.7	119,375	79,750	18.7	48.0
1575	40	Lead	1000	....	10	....	19.5	115,500	75,000	19.5	51.5
1575	40	Lead	1200	....	10	....	16.7	100,425	61,700	26.5	55.7
1575	40	Lead	650	....	2.5	....	24.2	125,775	85,200	20.2	53.8
1575	40	Lead	650	....	5.0	....	24.5	124,000	80,750	20.2	57.8
1575	40	Lead	650	....	10.0	....	23.5	127,200	83,500	15.6	40.8
1575	40	Lead	650	....	20.0	....	23.7	125,250	83,500	18.1	57.8

*These figures represent the averages of two or more bars.

Table III
Heat Treatment, Hardness and Charpy Impact Properties of a 0.34 Per Cent Carbon Steel*

Charpy bars 0.394-inch square. Key-Hole Notch

Quench Temp. Deg. Fahr.	Time at Temp.	Heating Time (Mins.)	Quench Medium	Temp. of Medium Deg. Fahr.	Temper Temp. Deg. Fahr.	Temper Time (Mins.)	Temper Medium	Rockwell "C" Hardness	Impact (Ft.-Lbs.)
1680	5	15	Oil	70	650	22.5	Lead	23.2	14.5
1680	5	15	Oil	70	800	22.5	Lead	16.0	20.7
1680	5	15	Oil	70	1000	22.5	Lead	13.0	23.5
1680	5	15	Oil	70	1200	22.5	Lead	10.2	24.7
1680	5	15	Water	70	650	22.5	Lead	38.5	21.0
1680	5	15	Water	70	800	22.5	Lead	31.0	26.5
1680	5	15	Water	70	1000	22.5	Lead	15.0	34.0
1680	5	15	Water	70	1200	22.5	Lead	8.0	44.7
1680	5	15	Lead	650	....	7.5	....	14.2	25.0
1680	5	15	Lead	800	....	7.5	....	12.8	29.0
1680	5	15	Lead	1000	....	7.5	....	7.3	30.0
1680	5	15	Lead	1200	....	7.5	....	4.0	31.0
1580	5	15	Oil	70	650	22.5	Lead	27.6	26.5
1580	5	15	Oil	70	800	22.5	Lead	22.8	28.5
1580	5	15	Oil	70	1000	22.5	Lead	17.0	34.5
1580	5	15	Oil	70	1200	22.5	Lead	9.0	39.5
1580	5	15	Lead	650	....	7.5	....	15.3	30.0
1580	5	15	Lead	800	....	7.5	....	12.2	36.5
1580	5	15	Lead	1000	....	7.5	....	6.5	43.0
1580	5	15	Lead	1200	....	7.5	....	4.0	44.5
1580	5	15	Water	70	650	22.5	Lead	28.6	18.5
1580	5	15	Water	70	800	22.5	Lead	23.8	31.0
1580	5	15	Water	70	1000	22.5	Lead	11.8	45.0
1580	5	15	Water	70	1200	22.5	Lead	5.0	50.2
1680	5	15	Lead	650	....	2.0	Lead	13.1	30.0
1680	5	15	Lead	650	....	3.7	Lead	16.3	30.5
1680	5	15	Lead	650	....	7.5	Lead	14.1	31.0
1680	5	15	Lead	650	....	15.0	Lead	13.0	31.0
1680	5	15	Lead	650	....	30.0	Lead	14.8	32.0
1725	5	15	Lead	650	....	3.7	Lead	15.3	28.0
1725	5	15	Lead	650	....	7.5	Lead	14.2	23.5
1580	5	15	Water	70	Not tempered	....	....	40.7	11.5
1580	5	15	Oil	70	Not tempered	....	....	29.5	40.0

*These figures represent the averages of two or more bars.

four impact bars (two samples tied together) were treated at one time.

The quenching and tempering time in the lead, given in Figs. 1, 2 and 3, is the total heating time the specimen was exposed and includes its "heating up" time as well as the time at temperature. Immersion of the samples was made after the lead had reached the tempering temperature. Owing to the large relative volume of the lead, there was no noticeable change in its temperature when specimens were introduced.

The heating and tempering cycles of the tensile and impact bars are based on the relative cross sectional area of the two test bars. The heating time for the tensile bars was 30 minutes with an additional 10 minutes at temperature, while the impact bars were

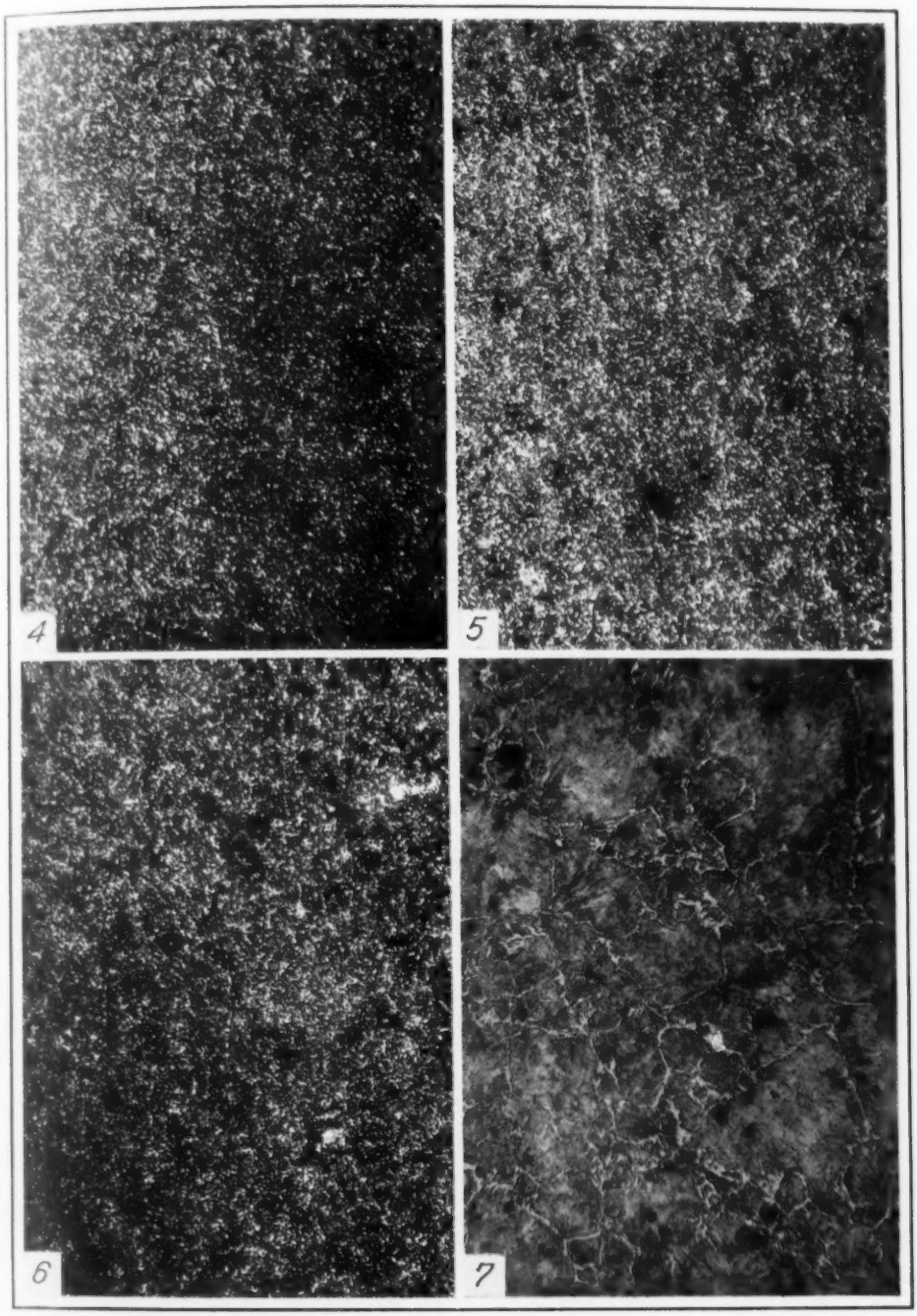


Fig. 4—Microstructure of 0.34 Per Cent Carbon Steel Quenched from 1680 Degrees Fahr. in Water at 70 Degrees Fahr. and Tempered in Lead at 1200 Degrees Fahr. for 22.5 Minutes. Sorbitic Structure. Etched in Picric Acid in Alcohol. × 100.

Fig. 5—Microstructure of 0.34 Per Cent Carbon Steel Quenched from 1580 Degrees Fahr. in Oil at 68 Degrees Fahr. and Tempered at 1200 Degrees Fahr. in Lead for 22.5 Minutes Then Cooled in Air. Sorbitic Structure. Etched in Picric Acid in Alcohol. × 100.

Figs. 6 and 7—Microstructures of 0.34 Per Cent Carbon Steel Quenched from 1580 Degrees Fahr. in Lead at 650 Degrees Fahr. and 1200 Degrees Fahr. Respectively, and Held for 7.5 Minutes Then Cooled in Air. These Photomicrographs Show a Slight Ferrite Network. × 100.

Figs. 6 and 4 are Representative of Steels Having Similar Mechanical Properties when Treated in ½-Inch Rounds.

Table IV
Heat Treatment, Hardness and Charpy Impace Properties of a 0.49 Per Cent Carbon Steel*

Charpy bars 0.394-inch square. Key-Hole Notch

Quench Temp. Deg. Fahr.	Time at Temp. (Mins.)	Quench Medium	Temp. of Medium Deg. Fahr.	Temper Temp. Deg. Fahr.	Temper Time (Mins.)	Temper Medium	Rock. "C" Hardness	Impact Values (Ft.-Lbs.)
1500	15	Water	70	650	22.5	Lead	42.8	11.5
1500	15	Water	70	800	22.5	Lead	36.9	29.0
1500	15	Water	70	1000	22.5	Lead	31.8	33.0
1500	15	Water	70	1200	22.5	Lead	21.7	39.0
1500	15	Oil	..	650	22.5	Lead	26.9	29.0
1500	15	Oil	..	800	22.5	Lead	25.1	32.5
1500	15	Oil	..	1000	22.5	Lead	23.6	37.0
1500	15	Oil	..	1200	22.5	Lead	17.2	43.0
1500	15	Lead	650	....	7.5	Lead	30.7	23.0
1500	15	Lead	800	....	7.5	Lead	26.3	26.5
1500	15	Lead	1000	....	7.5	Lead	20.2	30.0
1500	15	Lead	1200	....	7.5	Lead	14.8	36.0
1575	15	Water	70	650	22.5	Lead	45.2	11.0
1575	15	Water	70	800	22.5	Lead	39.6	21.5
1575	15	Water	70	1000	22.5	Lead	30.4	31.0
1575	15	Water	70	1200	22.5	Lead	20.8	41.0
1575	15	Oil	..	650	22.5	Lead	28.8	26.5
1575	15	Oil	..	800	22.5	Lead	25.2	27.0
1575	15	Oil	..	1000	22.5	Lead	23.2	30.0
1575	15	Oil	..	1200	22.5	Lead	17.1	33.5
1575	15	Lead	650	....	7.5	Lead	28.0	23.5
1575	15	Lead	800	....	7.5	Lead	22.8	26.0
1575	15	Lead	1000	....	7.5	Lead	19.3	28.0
1575	15	Lead	1200	....	7.5	Lead	12.5	29.0

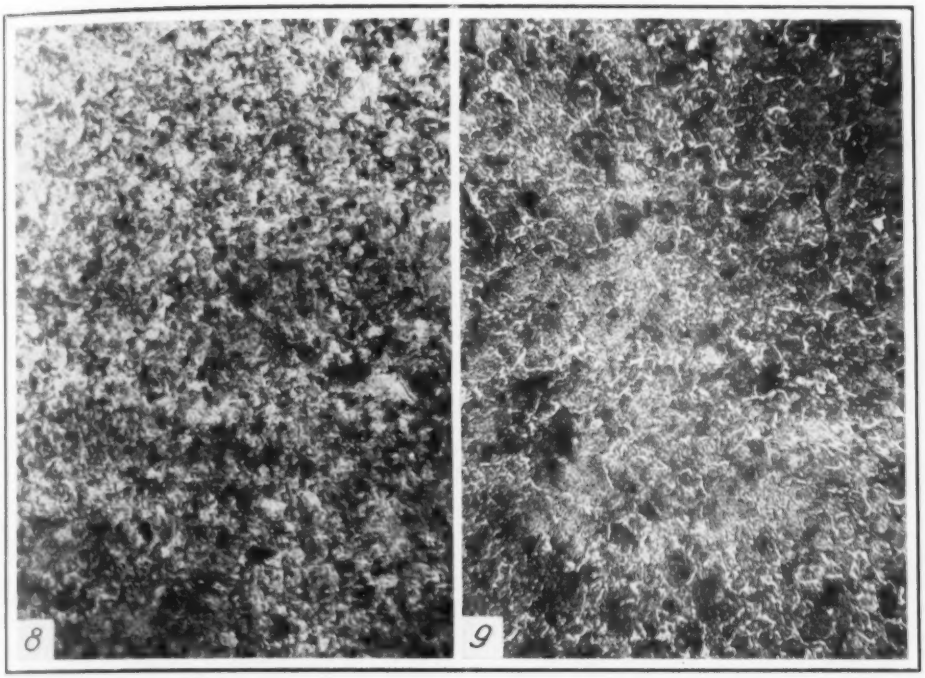
*These figures represent the averages of two or more bars.

brought to temperature in 15 minutes with a "soaking" period of 5 minutes. After removal from the lead, the samples were cooled in air while lying on a masonite bench and were not subject to air draughts. The properties shown in Tables I, II, III and IV, and in Figs. 1, 2 and 3, are based on the average properties of several specimens.

Summary of Results and Conclusions

This study brought out points which indicate that it might be of considerable interest and value to study further the use of molten lead baths for specific purposes.

In this particular investigation there was an insufficient number of samples of steel tested; second, carbon steels of various analyses were not tried; third, no alloy steels were used; fourth, the effect of quenching in lead from a larger number of temperatures should have been tried; fifth, the influence of the time of holding in the lead should be more extensively studied; sixth, the time-mass relationship in the lead requires more study; seventh, the influence of increasing the mass when quenching from a constant



Figs. 8 and 9—Steel Containing 0.49 Per Cent Carbon Quenched from 1500 Degrees Fahr. in Lead at 650 and 1200 Degrees Fahr. Respectively for 7.5 Minutes then Cooled in Air. The Effect of the High Lead Temperature Quench is Evidenced by the Ferrite Network Shown in Fig. 9. The Structures are Troostite Plus Sorbite and Sorbite Plus Network Ferrite Respectively. Etched in Picric Acid in Alcohol. × 100.

temperature might also be investigated further; and eighth, a comparison of the fatigue properties of the samples might also be advantageous. However, as shown in Tables I, II, III and IV, and in Figs. 1, 2 and 3, one definite characteristic may be found; namely, that a consistent and sequential series of mechanical properties result which show a variation with the temperature of the lead quench. This information may be utilized to advantage when specific sorbitic or troostitic structures are desired without risking breakage of the part treated. No cracks were found in any of the specimens quenched in either oil or lead.

No appreciable influence is evident on the tensile properties of these steels by prolonging the time of holding in the lead at 650 degrees Fahr. from 2½ to 20 minutes as shown in Tables I and II and in Fig. 1.

The tensile properties of the steel with 0.49 per cent carbon quenched from 1575 degrees Fahr. (860 degrees Cent.) in water and tempered at the usual commercial tempering temperature (900-1150 degrees Fahr.) are not greatly different from those specimens quenched in lead at 650 degrees Fahr. (345 degrees Cent.).

In conclusion, it may be stated that some practical aspects of this problem remain to be quantitatively solved. Additional factors, not mentioned previously, consist of such matters as cost, permanence, usable range, operator's safety, adherence of lead to the steel with a consequent loss and diminution of the bath which also in turn affects the cleaning costs, and others. In addition, it may be pointed out that a movement in the bath, though highly desirable because of the low convection in molten lead or other metals, is rendered somewhat difficult by their viscosity.

The number of factors which influence the product of a given heat treatment is greater in the case of cooling in molten metal than in the more common heat treatment operations, because, in addition to the usual variables—initial temperature, size, composition and cooling medium—others such as time of immersion and rate of movement while in the medium, are also introduced.

ACKNOWLEDGMENT

The assistance given by Miss C. H. Green and F. Teal is appreciated.

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THE DETERMINATION OF THE RATES OF GRAPHITIZATION AT 925 DEGREES CENT. IN TUNGSTEN-MANGANESE WHITE CAST IRON

By W. A. Pennington and W. H. Jennings

Abstract

Both manganese and tungsten have been found, by a metallographic investigation, to favor the formation of carbides when present in white cast iron. Manganese, in the absence of iron sulphide, has little effect upon the first stage of graphitization when not more than one per cent of the element is present. As the concentration of this element is increased from one per cent, the time for graphitization increases quite appreciably, reaching a maximum at about three per cent manganese. From three to five per cent the time decreases gradually. The effect produced by tungsten depends on the manganese content. Tungsten (up to five per cent), in the presence of one per cent manganese, slightly retards graphitization. It accelerates graphitization in alloys containing as much as 2.5 per cent manganese.

IN 1923, an intensive program was initiated in this laboratory to investigate the factors which influence the rates of malleabilization of white cast iron, as well as the properties of the annealed specimens. After the discovery of a shortened annealing cycle, it became evident that, by changing the composition, even a more rapid cycle might be obtained. This work led to the investigation of alloy white cast iron.

The purpose of this investigation was to ascertain the quantitative effects of manganese and various combinations of manganese and tungsten on the decomposition of iron carbide, Fe_3C, in commercial white cast iron.

Cast Iron Containing Manganese

A search of the literature reveals that many contributions have been made concerning the effect of manganese on the graphitization

Of the authors, Professor Jennings is instructor of physical chemistry at the Iowa State College and Mr. Pennington is associated with him. This manuscript is from a thesis submitted to the Graduate Faculty of Iowa State College in partial fulfillment of the requirement for the degree of Doctor of Philosophy. Manuscript received August 12, 1933.

of white cast iron. Much of this work has been of a qualitative nature. The quantitative data which have been obtained were for specimens containing relatively low percentages of the alloying element. No complete investigation has been made with a cast iron containing more than 2.11 per cent manganese.

The researches which have been done with these lower percentages of manganese reveal that manganese not only affects the rate of decomposition of the iron carbide, but it also has a destructive effect on any iron sulphide, that may be present, converting it to manganese sulphide. As shown by Hoelscher,[1] iron sulphide has an extremely marked deleterious influence on the rate of graphitization, while manganese sulphide appears to have little or no effect. The difference in the effects of the two compounds may be explained on the basis of the difference in their melting points. Levy[2] believes that iron sulphide forms films which envelop the grains of cementite, and consequently, because of their opposition to the expansion that accompanies graphitization, they retard the process. Manganese sulphide, on the other hand, forms little globules which are embedded in the matrix, and therefore have but little effect on the process. From the foregoing citations, it is obvious that, in correlating the available data, the effect of manganese on the rate of decomposition of iron carbide cannot be predicted unless iron sulphide be practically absent or its effect duly considered.

Since manganese, when present as manganese carbide, retards graphitization very appreciably and since manganese sulphide has little effect, the addition of a definite amount of sulphur will correct for the effect of manganese. Conversely, manganese may be added to correct for the harmful effect produced by sulphur when in the form of FeS. Evidently there must be some optimum ratio of manganese to sulphur. Hoelscher found that this ratio should be 4.6 for cast iron containing 2.10 per cent carbon and 5.4 for that containing 2.40 per cent carbon. Hoelscher quotes Gilmore as stating that the ratio manganese to sulphur should never be below 1.7 if good malleable iron is to be produced. Yemenidijian[3] states that, "the optimum percentage of manganese to balance the effect of sulphur in retarding graphitization is about twice the per cent of

[1]A. P. Hoelscher, Unpublished Thesis, Library, Iowa State College, Ames, Iowa (1930).

[2]Donald Levy, *Journal*, Iron and Steel Institute, Vol. 81, 1910, p. 403-23.

[3]M. K. Yemenidijian, Unpublished Thesis, Library, Iowa State College, Ames, Iowa, 1928.

sulphur plus 0.15 per cent manganese. This value is lower for high silicon alloys." The highest percentage of manganese in any of the alloys that Yemenidijian used was 0.66, while the maximum in those of Hoelscher was 0.397.

On the assumption that there is enough manganese to balance the effect of sulphur, any additional manganese will react with iron carbide by the equation,

$$Fe_3C + 3\ Mn = Mn_3C + 3\ Fe$$

The manganese carbide thus formed will remain in solid solution with the iron carbide. This cementite is by no ordinary means distinguishable from Fe_3C cementite. Manganese, in pure iron-carbon alloys, tends to increase the stability of the cementite, lowers the temperature of primary solidification and lowers the eutectic temperature slightly.[4] Guillet[5] states that manganese forms a double carbide which prevents graphitization. Manganese-iron-carbon alloys containing more than 0.8 per cent manganese are very brittle.[6] Osann[7] says that this defect can be removed by very slow cooling. On investigating the manganese-carbon system, Stadeler[8] found that manganese would absorb 3.6 per cent carbon at 1450 degrees Cent. (2640 degrees Fahr.) in one hour and 6.72 per cent at 2000 degrees Cent. (3630 degrees Fahr.) in the same length of time. He verified the belief that Mn_3C is brittle by immersing the hot alloys in water. Those which contained more than 3.0 per cent carbon immediately fell to pieces.

According to a curve, constructed or reproduced from the data of Sawamura by Coyle,[9] manganese, as well as carbide forming elements in general, raises the temperature of beginning graphitization. From this curve it may be noted that when the manganese content exceeds 2.5 per cent the temperature of beginning graphitization exceeds 980 degrees Cent. (1800 degrees Fahr.). The writers had no unusual difficulty in completely decomposing the free cementite in a cast iron containing 5 per cent manganese at 925 degrees Cent. (1700

[4] G. M. Enos, *Metals and Alloys*, Vol. 1, 1930, p. 595-601.

[5] Leon Guillet, *Revue de Metallurgie*, Vol. 5, 1908, p. 306-18.

[6] Cast iron bars which contained as much as 2.5 per cent manganese were exceptionally brittle. In fact, they were so brittle that much difficulty was had in obtaining the Brinell hardness due to the ease with which they fractured.

[7] Bernhard Osann, *Stahl und Eisen*, Vol. 30, 1910, p. 1918-21.

[8] A. Stadeler, *Metallurgie*, Vol. 5, 1908, p. 260-75.

[9] F. B. Coyle, *Metals and Alloys*, Vol. 2, 1931, p. 120-31.

degrees Fahr.). This apparent conflict may be explained by the fact that Sawamura progressively increased the temperature while the writers experimented at a constant temperature.

The effect of manganese in retarding graphitization in the first stage is well shown by the following data of Kikuta:[10]

Table I
Effect of Manganese in Retarding Graphitization

No. Specimen	Carbon	Silicon	Per Cent Manganese	Sulphur	Phosphorus	Time for First Stage at 925 Degrees Cent.
47	2.62	1.15	0.22	0.026	0.126	5 hours
40	2.51	1.15	0.46	0.033	0.127	5.5 hours
41	2.61	1.20	1.02	0.033	0.130	7 hours
42	2.64	1.12	1.26	0.024	0.136	8 hours
43	2.64	1.15	1.81	0.013	0.134	13 hours
44	2.72	1.15	2.11	0.022	0.128	22 hours
45	2.60	1.11	3.16	0.013	0.133	25 + X hours

Sample No. 45 suffered no graphitization after being heated for 25 hours at 925 degrees Cent. (1700 degrees Fahr.). Hayes and Flanders[11] found that manganese is much more effective at low than at high temperatures.

Cast Iron Containing Tungsten

The effect of tungsten upon graphitization in white cast iron has not been so carefully pursued as has the effect of manganese. A survey of the literature has revealed nothing more than qualitative data which are very much in disagreement.

Coyle[9] classes tungsten, along with nickel, aluminum, titanium, and copper, as graphitizing elements stating that, "These elements cause cementite to decompose into graphite and pearlite and possibly some ferrite." Schwartz[12] lists tungsten with columbium, platinum, gallium, palladium and tantalum as elements which have no measurable effect. In contradiction to these two views, Sawamura proposes that tungsten retards graphitization, although the effect is slight.

The system involving tungsten may be expected to be more complicated than that of manganese because it contains many more molecular species. According to Persoz,[13] tungsten goes into cementite

[10]Tario Kikuta, Science Reports, Tohoku Imperial University, Vol. 15, 1926, p. 115-55.

[11]Hayes and Flanders, *Transactions*, American Foundrymen's Assoc., Vol. 33, 1925, p. 634-38.

[12]H. A. Schwartz, *Foundry Trade Journal*, Vol. 39, 1928, p. 297-8.

[13]L. Persoz, *Foundry Trade Journal*, Vol. 40, 1929, p. 181-2.

forming a very stable complex carbide with iron. Sisco[14] states that tungsten reacts with both iron and carbon to form complexes whose general formula may be represented as x Fe_3C.yWC. He concludes that it is rather certain that tungsten carbide exists in tungsten cast iron, and that there are also probably such compounds as Fe_2W and Fe_3W present. In working with the tungsten-carbon system, Becker[15] concluded that WC forms and is stable up to 1900 degrees Cent. (3450 degrees Fahr.) at which temperature it decomposes into W_2C and carbon.

Using the dilatometric and magnetic methods, Takeda[16] has determined the equilibrium diagram of the tungsten-iron-carbon system. He finds that, in this system, there are two equilibrium diagrams. The Fe-C-WC is the stable system; the Fe-θ-η system is metastable. The θ-phase is a ternary solid solution composed chiefly of Fe_3C which decomposes on annealing to graphite and iron. The η-phase is also a ternary solid solution consisting mainly of a double carbide, Fe_3W_3C, which decomposes into WC and Fe. The excess tungsten probably unites with carbon from the θ-phase to form more WC.

Due to the great complexity of the tungsten-iron-carbon system, to say nothing of the complexity of the tungsten-iron-carbon-manganese-silicon system, it is difficult to predict the effect that would be produced upon the stability of Fe_3C when tungsten is introduced into cast iron.

Experimental Procedure and Data

A. Preparation of Alloys

The materials used in the preparation of the alloys used in this investigation consisted of commercial white cast iron test bars, ferromanganese, ferrotungsten and powdered graphite.

The white cast iron test bars, according to Henderson,[17] showed the following composition: Carbon, 2.60 per cent; silicon, 0.78 per cent; manganese, 0.20 per cent; sulphur, 0.034 per cent; phosphorus, 0.154 per cent. The ferromanganese contained about 80 per cent

[14]F. T. Sisco, Transactions, American Society for Steel Treating, Vol. 17, 1930, p. 111-29.

[15]Karl Becker, *Z. Metallkunde*, Vol. 20, 1920, p. 437-41.

[16]S. Takeda, Technical Reports, Tohoku Imperial University, Vol. 9, 1929-31, p. 627-64.

[17]E. L. Henderson, Unpublished Thesis, Library, Iowa State College, Ames, Iowa, 1931. Henderson and Jennings, *Metals and Alloys*, Vol. 2, 1931, p. 223-25.

manganese. The ferrotungsten, as reported by the manufacturer, was of the following composition: tungsten, 73.23 per cent; silicon, 0.42 per cent; carbon, 0.59 per cent; sulphur, 0.54 per cent; phosphorus, 0.015 per cent; manganese, 0.19 per cent.

3000 grams of the commercial white cast iron test bars were melted in a small plumbago crucible by means of a 35-kilowatt Ajax Northrup electric furnace. Twenty-five minutes after the run was started, carbon to the extent of one-tenth per cent of the total mass, and calculated amounts of ferromanganese and ferrotungsten were added to the molten metal. Immediately after this addition, the melt was stirred with an Armco rod. About ten minutes later, the melt was poured into wet sand molds. The molds containing the cast iron bars were permitted to stand for twenty-four hours before being broken. This period of time gave ample assurance that the bars of different compositions had the same cooling treatment. The pouring temperature, as determined by a Leeds and Northrup optical pyrometer, was in each case slightly above 1300 degrees Cent. (2370 degrees Fahr.).

B. Chemical Analyses

The chemical analyses were carried out according to the standards of the American Society for Testing Materials. Tungsten was determined by the acid-digestion cinchonine method in which the tungsten was finally weighed as WO_3. Manganese was determined by the sodium bismuthate method. Sulphur was determined gravimetrically by precipitating it as $BaSO_4$. Silicon was determined by the nitro-sulphuric and dehydration method. Since Henderson, using the same base metal, found that the sulphur content of seven different alloys was very close to constant at 0.035 per cent and since the writers found that four of these alloys, made from the same base metal, also contained 0.035 per cent sulphur, it was assumed that the other alloys would also contain very close to this same amount. Therefore, the sulphur determinations were made for only four of the twelve alloys. Likewise, it was deemed inadvisable to make the phosphorus determinations because other investigators, using the same base metal, found that the phosphorus content remained practically constant at 0.15 per cent. The carbon determinations were made by direct combustion in a stream of oxygen, ascarite being used as the absorbent. The analyses follow:

Table II
Analyses of Alloys

Melt No.	Carbon	Manganese	Per Cent Sulphur	Silicon	Tungsten
25	2.69	0.945	0.036	0.84	0.91
26	2.64	0.88	.....	0.845	2.78
27	2.53	0.89	.....	0.845	4.91
28	2.65	2.87	.....	0.85	0.87
29	2.59	2.64	.....	0.88	2.63
30	2.59	2.85	.....	0.845	4.27
31	2.66	4.59	.....	0.79	0.93
32	2.65	4.47	.....	0.789	2.65
33	2.58	0.95	0.034	0.84	....
34	2.80	3.28	0.035	0.84	....
35	2.84	5.01	0.035	0.83	....
36	2.61	4.26	.....	....	4.18

C. Heat Treatment

The heat treatment was made in a Hump annealing furnace at 925 degrees Cent. The temperature was determined by means of iron-constantan thermocouples and was controlled by a Leeds and Northrup automatic recorder. A Leeds and Northrup student potentiometer was used frequently to check the accuracy of the automatic recorder. In order to be more certain that the annealing temperature was known, the readings of the iron-constantan thermocouples were checked against a standard platinum-rhodium thermocouple. The iron-constantan thermocouples were replaced each 48 hours due to the oxidation of the iron.

As has been said, the purpose of this investigation was to determine the effects of manganese and tungsten on the rates of graphitization through the first stage. However, an attempt was made to carry the graphitization of a few of the samples through the second stage by cooling them slowly (after the first stage had been completed) from 925 to 704 degrees Cent. (1700-1300 degrees Fahr.) and, at this point, maintaining constant temperature. The commercial white cast iron, which was used as a reference standard, was completely malleableized after heating 9 hours at 925 degrees Cent. (1700 degrees Fahr.), cooling to 704 degrees Cent. (1300 degrees Fahr.) in 5 hours and heating 5 hours at the latter temperature. The samples containing manganese and some of those containing both manganese and tungsten, whose A_1 critical point was higher than 704 degrees Cent. (1300 degrees Fahr.), after having been heated a predetermined time at 925 degrees Cent, were similarly cooled to 704 degrees Cent. (1300 degrees Fahr.) in 5 hours and maintained at this temperature for 40 hours. None of the samples

except No. 33 showed any marked progress toward graphitization in the second stage. Consequently, in view of this fact and others which have previously been discussed, further efforts to graphitize these samples through the second stage were abandoned.

The samples, which were about one inch in length, were packed either in iron gas pipes capped on one end or in small plumbago crucibles with gas carbon of about 20 mesh. The gas carbon served in the production of a reducing atmosphere, which would prevent undue oxidation of the samples. The plumbago crucibles were soon found to be entirely unsatisfactory for the longer heat treatments and were used only for those samples requiring less than 20 hours. Due to their porosity oxygen from the air had a rather unlimited circulation around the specimens being heat treated. Those few alloys which were heated for about 100 hours in the plumbago crucibles were converted, in each case, into merely swollen masses of oxides, which in some cases still contained a small core of the original. On the other hand, the iron pipes were sufficient to preserve the samples even when heated for 200 hours. It was noted, however, even after all these precautions that considerable decarburization took place near the surface.

Since only the microscopical method was used to determine the end of graphitization, it was thought to be advisable to make preliminary study to ascertain the approximate time for completion of the process for each of the alloys. In order to do this, one sample of each of the alloys was packed in each of two iron gas pipes (2 x 8 inches) with gas carbon and then placed in the annealing furnace, which had previously attained the annealing temperature. After the pipes were placed in the furnace its temperature usually fell to about 775 degrees Cent. (1425 degrees Fahr.), finally regaining the former height after the expiration of some 30 minutes. The time at which the furnace was again at 925 degrees Cent. (1700 degrees Fahr.) was recorded as that of the beginning of heat treatment. One pipe, which will be designated as pipe No. 1, was taken from the furnace at the end of 24 hours and permitted to cool in air to room temperature. After the pipe with its contents were cooled, the samples were examined microscopically as will be explained in a later section of this paper. Those samples which still contained massive cementite were repacked in the same pipe and replaced in the furnace. Pipe No. 2 was removed at the end of 48 hours and its contents similarly inspected. As in the former case, those alloys which showed

the presence of massive cementite were repacked and returned to the furnace. This process of removing the pipes alternately every 24 hours continued until each specimen had been rendered completely void of free cementite.

Now having found the approximate time samples were packed in individual pipes (2 x 8 inches) or, if convenient, they were packed in groups in larger pipes and placed in the furnace. After continuing the heat treatment for approximately the same length of time as that found in the preliminary study and cooling as before, it was found that none of the samples contained massive cementite. Shorter heat treatments were made until, in each case, the samples contained free cementite. Successive runs were made until the actual time for completing the process was determined. About eight samples of each composition received this treatment to either determine or confirm the time necessary for the completion of the first stage of graphitization.

It is interesting to note the anomalous results which were obtained in the preliminary study. In Table III these values are contrasted with those finally determined. The final value is taken as a rough average of those values which are near the end-point. It should be pointed out again that in the preliminary treatment the samples were checked only each 24 hours. Consequently, the preliminary value for those samples which required less than 24 hours are omitted.

Table III
Time Required for First Stage Graphitization

Melt No.	Per Cent Tungsten	Per Cent Manganese	Time in Hours Preliminary	Time in Hours Final
25	0.91	0.94	...	12
26	2.78	0.87	...	17
27	4.91	0.89	...	24
28	0.86	2.87	192	93
29	2.61	2.63	144	65
30	4.26	2.85	120	53
31	0.92	4.59	144	68
32	2.64	4.47	144	62
33	....	0.95	...	8
34	....	3.28	192	93
35	....	5.01	168	78
36	4.17	4.26	72	46
cast	....	0.20	...	8

D. Microscopical Study

To determine the end-point of graphitization the samples were polished on a rough emery wheel to a depth of about ⅛ inch in order to insure the elimination of surface heterogeneity. After continuing

the polishing with less severe abrading agents until the sample was well free of scratches, the specimen was etched with sodium picrate which showed the presence or absence of massive cementite. This etch was removed on the polishing wheels and then a nitric acid-ethyl alcohol (5 per cent nitric acid by volume) etch was administered in order to determine the nature of the matrix which was in most cases martensitic. Extreme difficulty was experienced in successfully obtaining and retaining the latter etch with a clear, well defined structure. Many of the samples were over-etched in one second. This rapid etching is probably due to the presence of the manganese.

The alloys as cast, unlike ordinary white cast iron, did not contain pearlite. Melts 30, 32 and 36 contained chiefly austenite with some martensite. In fact, alloys 32 and 36 contained so much austenite that they hardly exerted any force upon a magnet. Alloy 30 had considerably less austenite, being chiefly martensitic. With the exception of alloy 33, the remaining alloys were martensitic. There was no great difference between alloy 33 and ordinary white cast iron. In all of the alloys, except alloy 33, portions could be found which showed marked dendritic segregation. With the exception of alloy 33, all of the alloys showed a martensitic matrix after being heat treated for the prescribed time.

Discussion of Results

Both manganese and tungsten have been found to favor the formation of carbides in white cast iron. Because of the presence of these carbides more time is required to graphitize samples containing either tungsten, manganese or both than for ordinary commercial white cast iron.

In plotting the time for completion of the first stage of graphitization against the combined percentages of manganese and tungsten curves as shown in Fig. 1 are obtained. The point of zero per cent of the alloying constituents is taken from the work of Hoelscher. Evidently this point may be much higher indeed as this investigator obtained no graphitization, on heating a sample containing nearly zero per cent manganese and zero per cent tungsten for 71 hours. Even though a point on the ordinate has not definitely been determined, the 71 hour-point is accepted because, as far as this discussion is concerned, it does not matter whether this point be at 100 hours or at an infinite number of hours. The point for 2.11 per cent manganese is taken from the data of Kikuta. The entire curve from

the ordinate to the maximum represents the effect of manganese in white cast iron. In fact, the whole curve with the exception of the portion for "alloys containing about one per cent manganese" may be considered for manganese cast iron containing no tungsten.

The point at zero per cent of the alloying element is very high because of the presence of sulphur in the form of FeS. Reference has already been made to the low melting point of this compound. Since it does melt at a lower temperature than the other constituents

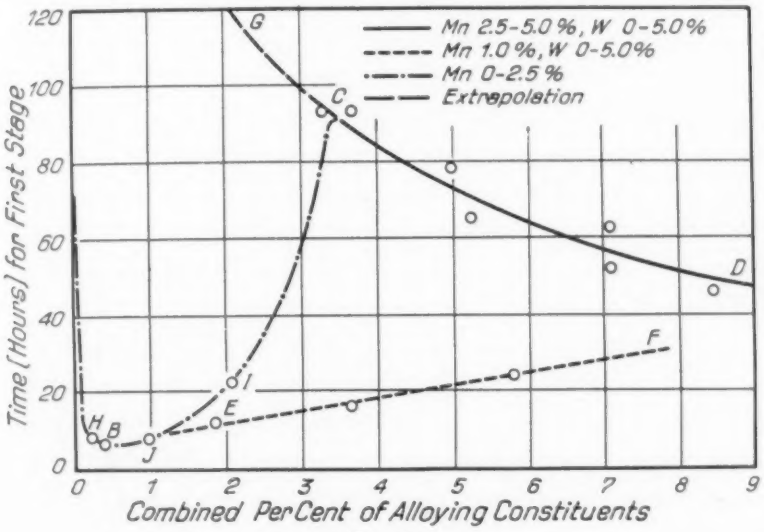


Fig. 1

of cast iron, it will be the last substance to solidify from the melt; therefore it will appear in the grain boundaries. In this position it serves as a film to prevent contact between the austenite and the cementite. As a result, the equilibrium,

$$Fe_3C \text{ (cementite)} = Fe_3C \text{ (dissolved)},$$

is impaired to such an extent that graphitization can take place only with great difficulty, if at all.

On increasing the manganese content from zero to 0.2 per cent the curve drops very rapidly. This part of the curve is due to the destruction of FeS from which MnS is formed. The manganese in forming the small sulphide globules, to which reference has been made, succeeds in destroying the film effect produced by FeS and permits graphitization to proceed. From 0.2 to 1.0 per cent manganese has but little effect on graphitization. As a matter of fact, the sample containing 0.2 per cent required exactly the same amount of time as the one containing 1.0 per cent. It is probable that this

part of the curve is due to the formation of some such compound as Mn_3P. There is no apparent reason why, if such a compound is formed, it should not behave similarly to Fe_3P. The formation of Mn_3P is assumed because it is definitely known that manganese will displace iron in FeS which would be indicative of the greater positivity of manganese. On increasing the manganese content above one per cent the curve makes a very steep rise which, of course, means that the effect of silicon is being compensated by the additional manganese. This retardation could be accomplished by isolation of the silicon in the form of MnSi or by the formation of a more stable carbide which would tend to reduce the amount of the unstable silico carbide present. The curve slopes gradually from the maximum as the percentage of manganese is increased. There are two ways of explaining this decrease in the time required: (1) The increasing manganese content serves to widen the austenitic area of the Fe-C equilibrium diagram, leaving less of the total carbides to decompose. (2) After the manganese has reacted with all of the impurities the system may be thought of as behaving more like the pure Fe-Mn-C system. If this is the case, CD represents a portion of the true Mn_3C line, and it appears that in these pure alloys manganese actually accelerates graphitization.

In support of this contention that manganese reacts with impurities other than sulphur, W. P. Fishel[18] finds that on treating a steel sample containing 0.6 per cent carbon and 0.7 per cent manganese with 3 per cent perchloric acid and analyzing the residue for manganese only 1.25 per cent remain. (Note: 0.7 per cent manganese is on the basis of the whole sample; 1.25 per cent is on the basis of the residue.) Since the residue is a comparatively small part of the whole, there is relatively little manganese in the residue. The above fact does not necessarily mean that the manganese is in the form of some compound such as those proposed, but may mean that a certain amount of Mn_3C in a state of subdivision was soluble in the acid. It does, however, point to the existence of manganese in the form of compounds other than the carbide and sulphide. A comparison of the tensile strength and hardness tests of the samples containing 1.0 per cent manganese with those containing 0.2 per cent indicates that the element is not entirely in the form of Mn_3C.[19]

[18]Private communication, (1932).

[19]The tensile strength and hardness of a sample containing one per cent manganese is almost identical with that of a sample containing 0.2 per cent.

In view of the assumption that these compounds form and that CD represents a portion of the Mn_3C line, it follows that the loop ABC is caused by the presence of the impurities, sulphur, phosphorus, and silicon. It has occurred to the writers that, if the amount of these impurities were decreased, this loop should be less pronounced, the minimum occurring considerably above and to the left of the minimum in Fig. 1. The maximum would occur at some point to the left of and higher than the maximum in Fig. 1 on DC extended. It will be noted that DC has been extended to approach the ordinate asymptotically.

The line CD shows that, regardless of the individual percentages of tungsten and manganese, the combined percentages of these elements is the factor which determines the time for graphitization. In other words, a sample containing 3 per cent manganese and 4 per cent tungsten will require the same length of time as a sample which either contains 5 per cent manganese and 2 per cent tungsten or 7 per cent of the former and zero per cent of the latter. Apparently when the manganese content is high enough to be at or to the right of the maximum on the curve, any additional tungsten acts like more manganese. If alloys were used containing 1.5 per cent manganese with varying amounts of tungsten, it is believed that a line above and parallel to the line, "Alloys containing about one per cent manganese," would be obtained. It is further predicted that an extension of these lines would coincide with CD after coming in contact with it. Any other series of alloys containing a constant amount of manganese would give a similar line the location of which would depend on the percentage of manganese.

It may be noted that on increasing the tungsten content from 0.91 to 4.91 per cent in the one per cent manganese alloys the time for graphitization doubles. This is probably a greater effect than the same amount of tungsten would have in an alloy containing approximately 0.2 per cent manganese. This assumption is made because of the belief that tungsten, on account of mass action, reacts with some of the compounds containing manganese and, thereby, allows more manganese to exist in the form of the carbide. There is but little doubt that tungsten will react with the impurities ordinarily found in white cast iron. In fact, Moissan[20] describes a compound that is formed when silicon and tungsten are heated together in an electric furnace. He states that the compound is crystalline

[20] H. Moissan, *Comptes rendus*, Vol. 123, 1896, p. 13-16.

with a metallic appearance and that it is hard enough to scratch ruby. This compound may account for some of the hardness caused by an addition of tungsten to cast iron. If tungsten reacts with silicon, it is logical to expect it to react also with sulphur and phosphorus since they are each more negative than silicon. A combination of tungsten with these elements would necessarily mean that more manganese could exist in the form of the carbide, which would tend to delay the graphitization more than would tungsten in the alloys having a lower manganese content.

Summary

1. The quantitative effect of manganese upon the rate of graphitization of white cast iron at a constant temperature (925 degrees Cent.) has been determined. The manganese content varied from 0.2 to 5.0 per cent.

2. The quantitative effect of a combination of tungsten and manganese upon the rate of graphitization at 925 degrees Cent. (1700 degrees Fahr.) in alloy cast iron, in which the tungsten varied from 0.87 to 4.91 per cent and the manganese varied from 0.88 to 4.59 per cent, has also been determined.

3. Manganese when added to commercial white cast iron has little effect on the first stage of graphitization until its content exceeds one per cent. From one to about three per cent it retards graphitization very strongly. As the amount is increased above three per cent, the time for complete graphitization is gradually reduced.

4. Tungsten in combination with one per cent manganese retards the first stage of graphitization slightly. When in combination with as much as about 2.5 per cent manganese, it serves to accelerate the process.

5. When the manganese content is 2.5 per cent, the same effect on the first stage of graphitization may be produced by addition of either more manganese or the same amount of tungsten.

6. White cast iron may be graphitized much more quickly at 925 degrees Cent. (1700 degrees Fahr.) by continuous heating than it can by interrupted heating. Specimens which required ordinarily 93 hours of continuous heating required 192 hours of heating in periods of 24 hours. At the end of each 24 hour period the samples were allowed to cool rather slowly to room temperature.

7. A curve obtained by plotting the time for complete graphitization in the first stage against the combined percentage of tung-

sten and manganese indicates that Fe_3C in pure Fe-C alloys is probably stable.

DISCUSSION

Written Discussion: By H. A. Schwartz, manager of research, National Malleable and Steel Castings Co., Cleveland.

This commentator finds much of interest in the paper by Drs. Pennington and Jennings, more especially because it constitutes an attempt to deal quantitatively with a quite complex system.

The authors have found it necessary in discussing their results to consider beside the two elements appearing in the title the elements silicon and sulphur which with the addition of the elements iron and carbon implicit in the problem, makes a system of at least six components and perhaps seven if phosphorus is to be considered in the manner proposed in the paper. It may be a little difficult to decide how many phases are to be assigned. Metallographically it is to be assumed that at 925 degrees Cent. (1700 degrees Fahr.) we would have at least graphite, a homogeneous solid solution (austenite or boydenite depending upon our choice of vocabulary and upon our understanding of the equilibria) and that constituent frequently called manganese sulphide which may, however, be a more complex substance. The authors assure us that the heat treatment was continued to the absence of free carbides else we might have to add an indefinite number of such substances. We thus appear to have equilibrium between six or seven components probably in three phases which at a given temperature and pressure leaves the system in an indeterminate condition thermodynamically. It is therefore apparent that the authors chose a decidedly difficult problem in which reproduceable results may be very hard to get.

In several cases the authors express views which may be regarded as somewhat unorthodox by many but which appear to the present writer to be entirely in accord with his own views and observations. For example, until very lately the crystallographic school of metallographers were prepared to abandon entirely the concept of molecules in homogeneous, solid or liquid solution. The validity of this generalization was never quite clear to the present writer and it was a pleasure to see that following long after the pioneers, Cesaro and von Jüptner, physical chemists as for example, Yap, Chu Phay and Körber and Oelsen have of late interpreted well known equilibrium diagrams as indicative of the presence of chemical compounds (Fe_3C in the cases referred to). The existence of manganese sulphide (so called) and its effect in undoing the harmful action of iron sulphide (also so called) in the graphitizing reaction has, of course, been admitted for we have metallographic evidence of the presence of this substance as an isolated phase.

The authors' sixth conclusion is most interesting to the writer. He can entirely support the observations which have been made and recorded in the paper that samples which are occasionally removed from the furnace for example and returned will require a longer time for graphitization than had the material been left at temperature continuously; many have expressed contrary

views, possibly Phillips and Davenport, "Malleableizing of White Cast Iron," *Transactions* of the American Institute of Mining and Metallurgical Engineers, Vol. LXVII, page 466, (1922) were the first to put forth the idea that fluctuations in temperature accelerated annealing. Later on presumably based on work done in the same laboratory as that in which the present authors are active a patent, No. 1574377, was granted to Dietrick and Hayes which seems to the writer to involve, especially in its claim 2, the assumption that oscillations of heat treatment are useful. Certainly the two pieces of laboratory work are in apparent conflict; whether both may be correct depending upon particular conditions is not properly a subject for discussion in the present connection. The commentator certainly feels that the observations of Pennington and Jennings are correct under the circumstances which they have recorded. In interpreting the authors' data much depends upon the degree of precision which may be claimed for their observations; unfortunately, we are given no details as to the time intervals at which specimens were removed from the furnace in the final series of observations; we cannot therefore, say how much of an error in time might be due to the particular intervals chosen for the experiment. For example, for a specimen to which an annealing time for complete graphitization is assigned the value fifty-three hours it would be very interesting to know what was the longest shorter time in which the anneal was observed to be incomplete. By the writer's methods we obviously cannot have precision greater than this last time interval. Incidentally, the present writer has always deplored the determination of the attainment of equilibrium at high temperature by metallographic means. The method does constitute a very accurate test for the effect of such attainment but is very insensitive to the time required to produce this condition.

There is probably general agreement that toward the end of the first stage of graphitization the time-combined carbon curve is for all practical purpose logarithmic in form, that is, the combined carbon decreases very slowly with increment of time. Now when cementite particles become small the chance of intersecting them in the metallographic plane is small and few of those existing will be found; even to find these is a considerable task to the metallographer. The net effect is usually to determine the equilibrium at too low a time due to failure to find the last traces of carbide. Now at the point where about one-half the graphitizable carbon has been destroyed the rate of destruction of graphite is very great and it has been shown by the present writer and his co-workers, "Graphitization at Constant Temperature," TRANSACTIONS, American Society for Steel Treating, Vol. 10, 1926, page 53, that chemical means applied when graphitization was about one-half complete furnished a very accurate means of determining graphitizing rate.

The writer regrets that in a paper of the present character a method was used for determining an essential factor with which it is so difficult to obtain perfectly accurate results even with the most careful work. Lacking specific statements as to the precision which the authors believe they have attained, we may refer to their Fig. 1 where in plotting the curve C-D they are quite willing to entertain departures up to eight hours in the case of individual points.

It must be confessed that one has found that the treatment of the data

from the viewpoint of the sum of the manganese and tungsten contents has proven somewhat difficult and confusing. The difficulty is in considerable part that when the data are so plotted it is obviously necessary to represent them by two different lines, one applied to a manganese content of 1 per cent and the other which the authors consider applicable to both of the higher manganese contents which they investigated. It is here that the question of precision enters; can we use a single line, C-D, or should a separate line be drawn for each of the two manganese contents? The factual knowledge which we actually have as the result of the present research is to be found in the thirteen observations comprised in Table III; with the exception of the last, these thirteen fall into three groups, the manganese being approximately constant within each of these groups.

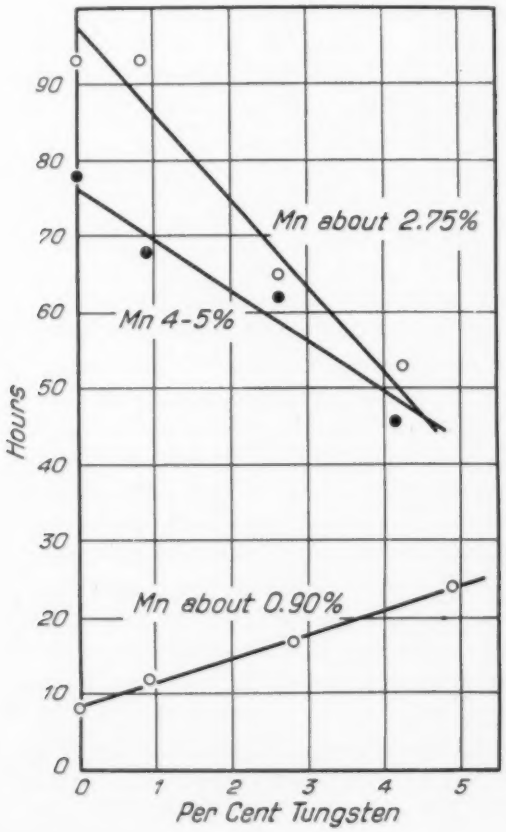
With a view to increasing his own understanding of the subject the writer has replotted the data of Table III in their logical subdivisions as the effect of tungsten on graphitizing time at constant manganese, the appropriate figure is shown on page 768.

The locus for approximately 1 per cent manganese is of necessity identical with the authors' E-F except for a shift of approximately 1 per cent at right angles to the time ordinate (i.e. a decrease of 1 per cent of alloying elements in the abscissae). It seems that each of the other two groups of constant manganese concentration can also be represented quite well by straight lines, the only question is a slight lack of concordance in the case of the two lowest tungsten concentrations at the intermediate manganese content. Even with this lack of concordance the straight lines agree with the observed points better than does the authors' line C-D. If this method of evaluation be adopted, then the effect of an increment in tungsten on annealing time is constant irrespective of its own concentration but the magnitude of this effect depends upon the concentration of manganese, thus for approximately 1 per cent manganese an increase of 1 per cent in tungsten increases the annealing time about three hours for the authors' alloys. For a manganese content of about 2½ or 2¾ per cent an increase of 1 per cent in tungsten decreases the annealing time eleven hours and at 4½ or 5 per cent manganese an increase of 1 per cent in tungsten decreases the annealing time to seven hours. No attempt has been made to see whether a better agreement could be obtained if the annealing rate (i.e. the reciprocal of the annealing time) were plotted as a rectilinear function of tungsten content. It seems rather unlikely that our data are sufficient to distinguish between these two postulates.

Now the annealing time could be plotted as a function of tungsten and manganese in a three-dimensional diagram in which the two elements are plotted on the system of rectangular coordinates on the base plane and the elevation of the surface above this base plane represents the time ordinate; the three lines just given represent at least approximately, lines of constant manganese content lying in this plane. In view of the irregularity of the effect of manganese both on the graphitizing time and on the rate of change of time with tungsten content, it seems hopeless to attempt to construct similar lines for constant tungsten and variable manganese. True we can construct such lines from Table III but each line will have but three points. Since they come no-

where near falling in a straight line they give us little to go on as to the form of curve which fits them best.

The authors are probably right in their analysis that excluding the effect of sulphur the curve is first approximately horizontal then rises and then falls but there seems to be no means of assigning it any definite form, possibly because we have no means of interpolation which we can reliably use between the observed points.



A very considerably greater number of observations suitably spaced would add materially to our ability to interpret the joint effect of the two elements and perhaps to sub-divide from one another those fields which the authors have suggested in their paper in discussing the joint effect of manganese, silicon and phosphorus.

In the light of the Figure which has been presented there may be some doubt as to whether it was reasonable to represent all of the alloys containing more than say 2.5 per cent manganese by a single line and if this doubt exists, then the treatment which the authors have used as the basis of their Fig. 1 becomes somewhat problematical.